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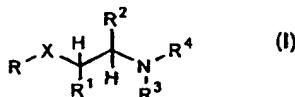
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(54) Title: SILICON CONTAINING COMPOUNDS



(57) Abstract: A silicon containing adduct having the formula (I) wherein X is an electron withdrawing group selected from the group consisting of carbonyl and sulphone groups, sulphonium and phosphonium salts; R is selected from the group consisting of hydrogen, linear and branched alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, di-alkylaminoalkyl, N-aryl-N-alkylaminoalkyl, hydroxylalkoxy, alkoxy, alkenyloxy, alkynyloxy, cycloalkoxy, cycloalkenyloxy, cycloalkynyoxy, aralkoxy, alkoxyaryloxy, alkoxyalkoxy, oligoalkoxyalkoxy, di-alkylaminoalkoxy, N-aryl-N-alkylamino-alkoxy, acyloxy, acyloxyalkyl, N-diacyl-iminoalkyl groups, organosilane, organosiloxane, hydroxyaryl, hydroxyalkenyl, hydroxyalkynyl and hydroxy groups and any of the above groups substituted with one or more hydroxyl or zwitterionic group Z, or R-X- is a nitrile group; R<sup>3</sup> and R<sup>4</sup> are individually selected from the group consisting of hydrogen, linear and branched alkyl, alkenyl, and alkynyl groups, aryl, alkoxy carbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the above groups substituted with a zwitterionic group Z, a hydroxyl group or an isocyanate group; R<sup>1</sup> and R<sup>2</sup> are individually selected from hydrogen and C<sub>1</sub>-C<sub>12</sub> alkyl groups; and at least one of groups R, R<sup>3</sup>, and R<sup>4</sup> contain an organosiloxane group Y and/or an organosilane group U. The invention additionally provides processes for the production of such an adduct, polymers formed therefrom, coating processes and compositions comprising an adduct or polymers produced therefrom.

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SILICON CONTAINING COMPOUNDS

It is well known in the literature that amines undertake nucleophilic attack on the  $\alpha,\beta$ -unsaturated carbonyl of an acrylate functionality, resulting in a Michael-type 1,4-adduct (*Recent stereoselective synthetic approaches 5 to -amino acids*. Cole, Derek C., *Tetrahedron* (1994), 50(32), 9517-82).

This technology has been applied in the preparation of a range of curable coatings (*Addition products, radiation-curable surface coating compositions based on the addition products, and their use for wood coating and paper coating*, Hintze-Bruning, Horst; Cibura, Klaus; Baltus, Wolfgang, 10 US 5792827; *High-solids coatings - formulation aspects*. Nowak, Michael T. USA. *High Solids Coat.* (1982), 7(3), 23-8) or resins (*Curing agents for liquid epoxy resins, and curable polymer compositions containing them*. Shiono, Kenji; Suzuki, Takehiro. JP 09291135; *A process for preparation of room-temperature-curable resins*. Furukawa, Hisao; Kawamura, Jo., EP 274112).

15 It has also been used extensively in polymer science, for example, to produce a variety of polymer hybrids (*Conductive wire coating based on a curable acrylate-modified amine-terminated polyamide*. Frihart, Charles R.; Kliwinski, Joseph. WO 9724191; *A polylactone having amino groups, its preparation, and coating and printing ink compositions containing it*. Matsui, 20 Hideki., EP 713894; *Grafting of amine-functional polymers onto functionalized oxymethylene polymers and the resulting graft polymers thereof*. Auerbach, Andrew B.; Broussard, Jerry A.; Yang, Nan L.; Paul, James L. EP 400827) or to build dendrimer structures (*Dense star polymers*. Tomalia, Donald A.; Dewald, James R. WO 8402705).

25 It can also be used to functionalise biologically active amine-bearing compounds (*A synthesis of N-substituted -alanines: Michael addition of amines to trimethylsilyl acrylate*. Kwiatkowski, Stefan; Jeganathan, Azhwarsamy; Tobin, Thomas; Watt, David S. *Maxwell H. Synthesis* (1989), Issue 12, 946-9).

30 The reaction may be carried out with either acrylate or methacrylate, although the former is generally preferred in the literature on reactivity grounds. The reaction proceeds usually without catalysis, although there

are reports of catalysts to promote solely 1,4 addition in good yields (Catalysis of the specific Michael addition: the example of acrylate acceptors. Cabral, Jose; Laszlo, Pierre; Mahe, Loic; Montaufier, Marie Therese; Randriamahefa, S. Lalatiana., *Tetrahedron Lett.* (1989), 30(30), 5 3969-72).

In EP-A-0230342 acrylic functional silicone compounds are synthesised by reaction of amine functional silicones with diacrylate compounds. To prevent both acrylate groups of the diacrylate reacting to crosslink the silicone, a monomeric acrylate or an anhydride is added to 10 block further reaction of the diacrylate with amine groups having reactive hydrogen atoms. Other disclosures of using diacrylates to crosslink aminefunctional silicones are made in EP-A-0933399, in which monomeric methacrylates including zwitterionic compounds may also be reacted with amine groups.

15       Silicone prepolymers have been used in the production of extended wear contact lenses, in processes in which they are copolymerised with hydrophilic and hydrophobic comonomers, with cross-linking agent, to give lenses which are very oxygen permeable, for instance in US-A-5760100. The silicone prepolymers generally comprise sequentially linearly linked 20 siloxane blocks, hydrophilic blocks and ethylenic blocks, with a variety of linking moieties. In EP-A-0455585 ethylenic unsaturation is introduced into amine functional silicones by reaction of the silicone with an isocyanate-functional ethylenic compound.

25       Phospholipids are phosphate diester compounds, naturally found in the cell membrane, in which one of the alcohol residues is generally a glycerol derivative, and the other is a derivative of a different alcohol which may include a non-ionic, cationic or even an anionic functionality.

Phospholipid and phospholipid analogues are of increasing interest, for example to impart the useful properties of biocompatibility, 30 haemocompatibility and to influence the interaction of surfaces with biomolecules such as proteins or enzymes.

Our previous disclosures such as EP-A 0032622, EP-A- 0157469, EP-A-0555295, EP-A-0601041, EP-A-0593561, EP-A- 00639989, WO-A-9416748 and WO-A-9416749 describe various synthetic zwitterionic compounds including phospholipid analogues and their application in devices having biocompatible and haemocompatible surfaces.

In particular, the present invention relates to new polymers, processes for producing them, processes for coating surfaces with them and polymer compositions. The invention also provides new prepolymers and processes for their production.

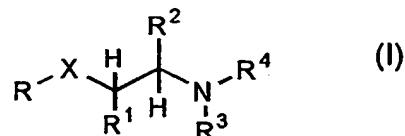
Such polymers are particularly useful in the manufacture or coating of devices with medical applications such as blood contacting devices, contact and intraocular lenses, and other devices which are used in contact with protein-containing or biological fluids.

The design of materials for biological or medical applications necessitates that a number of strict material requirements be met. For example, the design of contact lenses necessitates that the material must be optically transparent even after autoclaving, possess chemical stability, have suitable mechanical properties (low modulus of elasticity for patient comfort, adequate tear strength for handling), be biocompatible and have a sufficient water content so that the lens is wettable by tears and moves freely over the eye. In addition, because of lack of blood vesicles in cornea, the lens must be permeable to oxygen directly from the atmosphere. It is also important that the material can be polymerised using present contact lens manufacturing techniques. This normally involves the free radical initiated casting of methacrylate functional monomers, particularly hydrophilic monomers, to form water-swellable hydrogels. These many and often contradictory requirements have most conveniently been met using materials containing, for example, polydimethylsiloxane (PDMS) and polyether compounds.

Polydimethylsiloxane based materials are well known to have low modulus of elasticity, excellent transparency and high oxygen permeability. However, PDMS is completely non wettable by tears and exhibits are high

affinity for lipids with poor wetting and lens adhesion. Simple blending of PDMS or methacrylate functionalised PDMS with hydrophilic monomers tends to give rise to incompatibility and phase-separated opaque materials exhibiting poor mechanical properties.

5 The present invention provides a silicon containing Michael-type adduct having the formula (I)



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wherein

X is an electron withdrawing group selected from the group consisting of carbonyl and sulphone groups, sulphonium and phosphonium salts;

15 R is selected from the group consisting of hydrogen, linear and branched alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, di- alkylaminoalkyl, N-aryl-N-alkylaminoalkyl, hydroxyalkoxy, alkoxy, alkenyloxy, alkynyoxy, cycloalkoxy, cycloalkenyloxy, cycloalkynyoxy, aralkoxy, alkoxyaryloxy, alkoxyalkoxy, oligoalkoxyalkoxy, di-alkylaminoalkoxy, N-aryl-N-alkylamino-20 alkoxy, acyloxy, acyloxyalkyl, N-diacyl-iminoalkyl groups, organosilane, organosiloxane, hydroxyaryl, hydroxyalkenyl, hydroxyalkynyl and hydroxy groups and any of the above groups substituted with one or more hydroxyl or zwitterionic groups Z, or R-X- is a nitrile group;

25 R<sup>3</sup> and R<sup>4</sup> are independently selected from the group consisting of linear and branched alkyl, alkenyl, and alkynyl groups, aryl, alkoxy carbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl, N-30 diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the

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above groups substituted with a zwitterionic group Z, an isocyanate group, a hydroxyl group or a polymerisable ethylenically unsaturated group;

R<sup>1</sup> and R<sup>2</sup> are independently selected from hydrogen and C<sub>1</sub>-C<sub>12</sub> alkyl groups; and

5 a first group selected from R, R<sup>3</sup>, and R<sup>4</sup> contains an organosiloxane group Y and/or an organosilane group U,

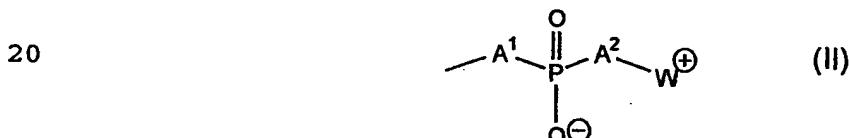
a second group selected from R, R<sup>3</sup> and R<sup>4</sup> is a hydrophilic group, and

the third group selected from R, R<sup>3</sup> and R<sup>4</sup> comprises a polymerisable ethylenically unsaturated group or an isocyanate group.

10 In the definition of R, R<sup>3</sup> and R<sup>4</sup>, any alkyl group or moiety is preferably C<sub>1-18</sub> alkyl, any alkenyl group or moiety is preferably C<sub>2-18</sub> alkenyl, any alkynyl group or moiety is preferably C<sub>2-12</sub> alkynyl, any aryl group or moiety is preferably C<sub>6-24</sub> aryl, any alkaryl group or moiety is preferably C<sub>7-24</sub> alkaryl and any aralkyl group or moiety is preferably C<sub>7-24</sub> aralkyl, any

15 cycloalkyl group or moiety is preferably C<sub>4-24</sub> cycloalkyl, any cycloalkenyl group or moiety is preferably C<sub>5-24</sub> cycloalkenyl, any cycloalkynyl group or moiety is preferably C<sub>5-24</sub> cycloalkynyl.

A zwitterionic group Z preferably has the general formula (II)



in which the moieties A<sup>1</sup> and A<sup>2</sup>, which are the same or different, are -O-, -S-, -NH- or a valence bond, preferably -O-, and W<sup>+</sup> is a group comprising an ammonium, phosphonium or sulphonium cationic group and a group linking the anionic and cationic moieties which is preferably a C<sub>1-12</sub>-alkanediyl group,

preferably in which W<sup>+</sup> is a group of formula

30 -W<sup>1</sup>-N<sup>+</sup>R<sup>5</sup><sub>3</sub>, -W<sup>1</sup>-P<sup>+</sup>R<sup>6</sup><sub>3</sub>, -W<sup>1</sup>-S<sup>+</sup>R<sup>8</sup><sub>2</sub> or -W<sup>1</sup>-Het<sup>+</sup> in which:

W<sup>1</sup> is alkanediyl of 1 or more, preferably 2-6 carbon atoms optionally containing one or more ethylenically unsaturated double or triple bonds, disubstituted-aryl (arylene), alkylene arylene, arylene alkylene, or alkylene

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aryl alkylene, cycloalkanediyl, alkylene cycloalkyl, cycloalkyl alkylene or alkylene cycloalkyl alkylene, which group W<sup>1</sup> optionally contains one or more fluorine substituents and/or one or more functional groups; and

either the groups R<sup>5</sup> are the same or different and each is hydrogen or

5 alkyl of 1 to 4 carbon atoms, preferably methyl, or aryl, such as phenyl, or two of the groups R<sup>5</sup> together with the nitrogen atom to which they are attached form an aliphatic heterocyclic ring containing from 5 to 7 atoms, or the three groups R<sup>5</sup> together with the nitrogen atom to which they are attached form a fused ring structure containing from 5 to 7 atoms in each

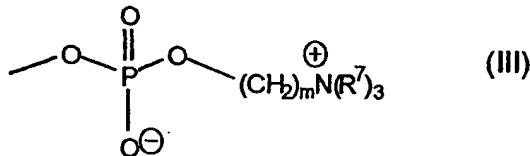
10 ring, and optionally one or more of the groups R<sup>5</sup> is substituted by a hydrophilic functional group, and

the groups R<sup>6</sup> are the same or different and each is R<sup>5</sup> or a group OR<sup>5</sup>, where R<sup>5</sup> is as defined above; or

15 Het is an aromatic nitrogen-, phosphorus- or sulphur-, preferably nitrogen-, containing ring, for example pyridine.

Most preferably the zwitterionic group of the formula (II), has the general formula (III):

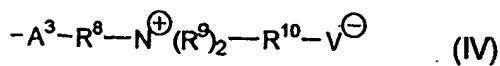
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where the groups R<sup>7</sup> are the same or different and each is hydrogen or C<sub>1-4</sub> alkyl, and m is from 1 to 4, in which preferably the groups R<sup>7</sup> are the same preferably methyl.

25 Alternatively, the zwitterionic group may be a betaine group (i.e. in which the cation is closer to the backbone), for instance a sulpho-, carboxy- or phospho-betaine. A betaine group should have no overall charge and is preferably therefore a carboxy- or sulpho-betaine. If it is a phosphobetaine the phosphate terminal group must be a diester, i.e., be esterified with an

30 alcohol. Such groups may be represented by the general formula (IV)



in which  $A^3$  is a valence bond, -O-, -S- or -NH-, preferably -O-;

$V$  is a carboxylate, sulphonate or phosphate diester(monovalently charged) anion;

5  $R^8$  is a valence bond (together with  $A^3$ ) or alkanediyl, -C(O)alkylene- or -C(O)NHalkylene preferably alkanediyl, and preferably containing from 1 to 6 carbon atoms in the alkanediyl chain;

the groups  $R^9$  are the same or different and each is hydrogen or alkyl of 1 to 4 carbon atoms or the groups  $R^9$  together with the nitrogen to which they are attached form a heterocyclic ring of 5 to 7 atoms; and

10  $R^{10}$  is alkyanediyI of 1 to 20, preferably 1 to 10, more preferably 1 to 6 carbon atoms.

One preferred sulphobetaine group has the formula (V)

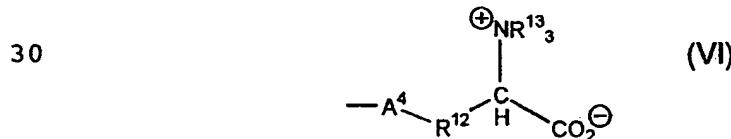


where the groups  $R^{11}$  are the same or different and each is hydrogen or  $C_{1-4}$  alkyl and  $s$  is from 2 to 4.

20 Preferably the groups  $R^{11}$  are the same. It is also preferable that at least one of the groups  $R^{11}$  is methyl, and more preferable that the groups  $R^{11'}$  are both methyl.

Preferably  $s$  is 2 or 3, more preferably 3.

25 Alternatively the zwitterionic group may be an amino acid moiety in which the alpha carbon atom (to which an amine group and the carboxylic acid group are attached) is joined through a linker group to the backbone of the biocompatible polymer. Such groups may be represented by the general formula (VI)



in which  $A^4$  is a valence bond, -O-, -S- or -NH-, preferably -O-,

$R^{12}$  is a valence bond (optionally together with  $A^4$ ) or alkanediyl, -C(O)alkylene- or -C(O)NHalkylene, preferably alkanediyl and preferably containing from 1 to 6 carbon atoms; and

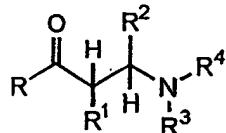
5 the groups  $R^{13}$  are the same or different and each is hydrogen or alkyl of 1 to 4 carbon atoms, preferably methyl, or two or three of the groups  $R^{13}$ , together with the nitrogen to which they are attached, form a heterocyclic ring of from 5 to 7 atoms, or the three group  $R^{13}$  together with the nitrogen atom to which they are attached form a fused ring heterocyclic structure containing from 5 to 7 atoms in each ring.

10  $R^1$  and  $R^2$  are preferably selected from hydrogen or  $C_1$ - $C_4$  alkyl groups, most preferably both hydrogen.

Most preferably the zwitterionic group is an ethylene-2-(trimethylammonium)ethylphosphate inner salt.

$X$  is preferably a carbonyl group and adduct (I) has the formula

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20  $R$  preferably is a group selected from a group substituted by a zwitterionic group  $Z$ , hydroxyalkoxy, hydroxy and poly(oxyalkyl)oxy, most preferably hydroxyalkoxy.

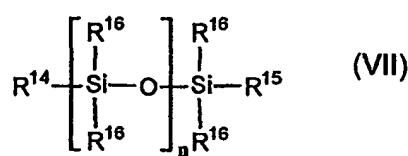
When  $R$  comprises a zwitterionic group  $Z$ ,  $R$  is preferably -OR', where R' is alkyl or aryl with substituents selected from groups (II), (III), (IV) and (VI).

25 Generally groups  $R$ ,  $R^3$ , and  $R^4$  have formula weights in the range 30-20,000.

When  $R$  contains a zwitterionic group,  $R$  preferably has a molecular weight in the range 150-400.

30 An organosiloxane group  $Y$  utilised in the present invention, for example as  $R$ ,  $R^3$  or  $R^4$ , preferably has the formula (VII)

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5 in which

$\text{R}^{14}$ ,  $\text{R}^{15}$  and each  $\text{R}^{16}$  are independently selected from monovalent groups selected from hydrogen, branched and straight  $\text{C}_{1-12}$  alkyl,  $\text{C}_{6-18}$  aryl,  $\text{C}_{6-18}$  alkaryl,  $\text{C}_{6-18}$  aralkyl,  $\text{C}_{2-12}$  alkenyl,  $\text{C}_{2-12}$  alkynyl and  $(-\text{OSiR}^{16})_p\text{OSiR}^{16}$ , and divalent groups selected from a valence bond, branched and straight  $\text{C}_{1-12}$ -alkanediyl,  $\text{C}_{6-18}$ -arylene,  $\text{C}_{7-18}$ -alkarylène,  $\text{C}_{12-2}$ -alkanediyl and  $\text{C}_{12-2}$ -alkynediyl, any of which may be substituted by a primary, secondary or tertiary amine group and/or a group  $\text{XCH}(\text{R}^1)\text{CH}(\text{R}^2)\text{NR}^3\text{R}^4$  or a group  $-\text{N}(\text{R}^3)\text{CH}(\text{R}^2)\text{CH}(\text{R}^1)\text{XR}$

10  $n$  is 0-300 and,15  $p$  is 0 to 50,

provided that at least one of the groups  $\text{R}^{14}$ ,  $\text{R}^{15}$  and  $\text{R}^{16}$  is a divalent radical which is covalently bonded to the rest of the molecule I. (VII) has a formula weight of 300-20000 Da, preferably 1000-7000, most preferably 3000-6000.

20 Where  $\text{R}$  is (VII), it is preferably connected to group  $\text{X}$  via the  $\text{R}^{14}$  or  $\text{R}^{15}$  group, preferably the  $\text{R}^{14}$  group. Where this is the case, another of the groups  $\text{R}^{14}-\text{R}^{16}$ , preferably  $\text{R}^{15}$ , may be connected to another group -  $\text{XCH}(\text{R}^1)\text{CH}(\text{R}^2)\text{NR}^3\text{R}^4$ . Alternatively, or in addition to  $\text{R}^{15}$  being connected to another such group, another of  $\text{R}^{14}$  to  $\text{R}^{16}$  may comprise an amine group, e.g. 25 a  $-\text{NH}_2$ ,  $-\text{NH}(\text{R}^{17})$  or  $-\text{N}(\text{R}^{17})_2$  group, wherein the or each  $\text{R}^{17}$  is selected from linear and branched alkyl, alkenyl, and alkynyl groups, aryl, alkoxy carbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl,  $\text{N-aryl-N-}$  30 alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl,  $\text{N-}$  diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the

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above groups substituted with a zwitterionic group Z an isocyanate group, a hydroxyl group or a polymerisable ethylenically unsaturated group.

Preferably  $R^{17}$  is  $C_{1-4}$ -alkyl

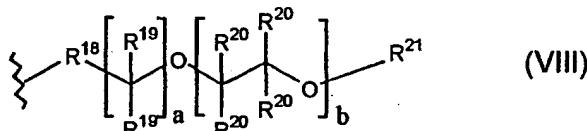
Preferably, each  $R^{16}$  is selected from the group consisting of  $C_{1-6}$  alkyl groups, preferably  $C_{1-4}$  alkyl groups, most preferably methyl. Preferably the groups  $R^{16}$  are the same.

Where  $R^4$  comprises (VII), (VII) is preferably connected to the nitrogen atom of adduct (I) through group  $R^{14}$  or  $R^{15}$ . Preferably the other of  $R^{14}$  and  $R^{15}$  is a group having a substituent  $-N(R^3)CH(R^1)CH(R^2)XR$ .

10 Preferably  $R^{14}$  is selected from methanediyl, ethanediyl, propanediyl and butanediyl.

Preferably  $R^{15}$  is either  $C_{1-4}$ -alkyl or  $C_{1-4}$ -alkyl substituted by a group  $-N(R^3)CH(R^1)CH(R^2)XR$ , preferably  $R^3$ ,  $R^1$ ,  $R^2$ , X and R having the same meanings as such groups in the core part of the molecule of the formula I.

15 An oligo(alkoxy)alkyl or a hydroxyalkyl oligo(oxyalkyl) group which is  $R^3$  or  $R^4$  may have the formula (VIII)



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in which

$R^{18}$  is a divalent group selected from a valence bond,  $C_{61}$ -alkanediyl,  $C_{2-6}$ -alkendiyl,  $C_{6-18}$ -arylene,  $C_{7-18}$ -alkarylene, and  $C_{1-6}$ -alkylamino  $C_{1-6}$  alkyl, any of which may be substituted by an amino group,

25 each group  $R^{19}$  and  $R^{20}$  is independently selected from the group consisting of hydrogen,  $C_{1-6}$  alkyl,  $C_{6-18}$  aryl,  $C_{6-18}$  aralkyl,  $C_{6-18}$  alkaryl and  $C_{2-6}$  alkenyl;

30  $R^{21}$  is selected from the group consisting of hydrogen,  $C_{1-6}$  alkyl,  $C_{6-18}$  aryl,  $C_{6-18}$  aralkyl,  $C_{2-6}$  alkenyl, aminoalkyl, mono-, di- and tri- alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl or any of the above groups substituted with a primary, secondary or tertiary amine group or a group  $N(R^3)CH(R^2)CH(R^1)XR$ ;

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a is an integer in the range of 0-10, provided that  $a \geq 1$  when  $R^{18}$  is a valence bond

b is an integer in the range of 1-500, and

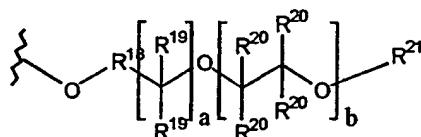
(VIII) has a formula weight of 100-10000.

5 Each group  $R^{19}$  is preferably selected from hydrogen or  $C_{1-4}$  alkyl, more preferably hydrogen or methyl. Each group  $R^{20}$  is preferably selected from hydrogen or  $C_{1-4}$  alkyl, more preferably hydrogen or methyl, most preferably H. For instance one of the groups  $R^{20}$  may be a methyl and the rest hydrogen, but most preferably all  $R^{20}$  groups are hydrogen.

10 Preferably (VIII) has a formula weight in the range 300-10000, more preferably 400-7000, more preferably 500-6000, most preferably 500-2000.

An oligo(alkoxy)alkoxy group R has the formula

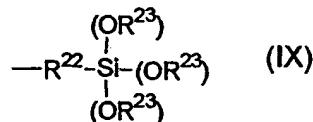
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wherein the groups  $R^{18}$  to  $R^{21}$  a and b have the same meanings as in VIII.

Preferably  $R^4$  is a polysiloxane represented by (VII),  $R^3$  comprises an ethylenically unsaturated group, and R is a hydrophilic group, for instance a 20 group comprising a zwitterionic group Z, more preferably a zwitterionic group (III), a  $C_{1-12}$  hydroxyalkoxy group or a group of formula V(III).

Where one of R,  $R^3$  and  $R^4$  does not contain an organosiloxane group, at least one of R,  $R^3$  and  $R^4$  is an organosilane group U. A preferred organosilane group for use in the present invention has the general formula 25 (IX)



30 wherein

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each R<sup>23</sup> is selected from the group consisting of hydrogen, branched and straight C<sub>1-12</sub> alkyl, C<sub>6-18</sub> aryl, C<sub>6-18</sub> alkaryl, C<sub>6-18</sub> aralkyl, C<sub>2-12</sub> alkenyl and C<sub>2-12</sub> alkynyl; and

5 R<sup>22</sup> is selected from the group consisting of a valence bond, branched and straight chain C<sub>1-12</sub> alkanediyl, straight and branched C<sub>2-12</sub> alkenediyl and straight and branched C<sub>2-12</sub> alkynediyl.

Preferably each R<sup>23</sup> is C<sub>1-4</sub> alkyl, preferably the same alkyl group.

Preferably R<sup>22</sup> is a C<sub>1-6</sub> alkanediyl, more preferably C<sub>1-4</sub> alkanediyl, most preferably 1,3-propanediyl.

10 An organosilane group (IX) preferably has a formula weight in the range 100-350.

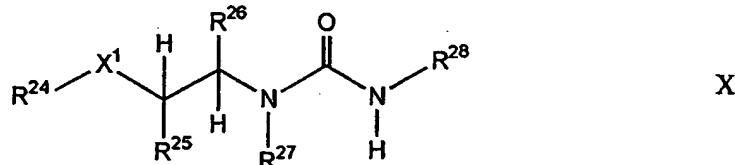
In a preferred embodiment in which the adduct is a prepolymer or macromer R<sup>3</sup> comprises an ethylenically unsaturated group or an isocyanate group that is capable of polymerising with comonomers. Such reactive 15 groups may additionally allow derivatisation of the adduct by conjugation to drugs, ligands or biological molecules such as enzymes or heparin.

Where R<sup>3</sup> comprises an ethylenic group, such a group is preferably selected from the group consisting of (meth)acryloyloxy, (meth)acrylamido and allyl groups.

20 Where R<sup>3</sup> comprises an isocyanate substituent R<sup>3</sup> is preferably a cycloalkylaminocarbonyl, arylaminocarbonyl, or alkylaminocarbonyl group containing an isocyanate substituent.

In a further aspect of the invention there is provided a compound of the general formula

25



30 in which X<sup>1</sup> is an electron withdrawing group selected from the group consisting of carbonyl and sulphone groups, sulphonium and phosphonium salts;

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$R^{24}$  is selected from the group consisting of hydrogen, linear and branched alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, di- alkylaminoalkyl, N-aryl-N-alkylaminoalkyl, hydroxyalkoxy, alkoxy, alkenyloxy, alkynyloxy, 5 cycloalkoxy, cycloalkenyloxy, cycloalkynyloxy, aralkoxy, alkoxyaryloxy, alkoxyalkoxy, oligoalkoxyalkoxy, di-alkylaminoalkoxy, N-aryl-N-alkylamino-alkoxy, acyloxy, acyloxyalkyl, N-diacyl-iminoalkyl groups, organosilane, organosiloxane, hydroxyaryl, hydroxyalkenyl, hydroxyalkynyl and hydroxy groups and any of the above groups substituted with one or more hydroxyl or 10 zwitterionic groups Z or  $-R^{24} X^1$  is a nitrile group;

$R^{25}$  and  $R^{26}$  are independently selected from hydrogen and  $C_1-C_{12}$  alkyl groups;

$R^{27}$  is an optionally substituted alkyl, alkenyl, alkynyl, aryl, cycloalkyl, cycloalkenyl or cycloalkynyl group; and

15  $R^{28}$  is an optionally substituted alkyl, alkenyl, alkynyl, aryl, cycloalkyl, cycloalkenyl or cycloalkynyl group.

$X^1$  is preferably a carbonyl group.

$R^{24}$  is preferably a hydrophilic group, more preferably selected from a zwitterionic or hydroxyl substituted alkoxy, alkoxyalkoxy or 20 oligoalkoxyalkoxy group. A zwitterionic group is preferably a group Z as defined in relation to the first aspect of the invention.

$R^{25}$  and  $R^{26}$  are preferably selected from hydrogen or  $C_1-C_4$  alkyl groups, most preferably both are hydrogen.

25 Optional substituents in  $R^{27}$  and  $R^{28}$  are preferably selected from hydroxyl, alkoxy, acyl, acyloxy, acylamino, isocyanate, amine, zwitterions, aryl, alkenylaryl and alkenyloxy groups and may comprise polymeric moieties.

One group of compounds of the general formula X comprises 30 polymerisable compounds, in which one of the groups  $R^{24}$ ,  $R^{27}$  and  $R^{28}$  comprises a polymerisable group, preferably selected from an ethylenically unsaturated group, an isocyanate or an active hydrogen containing group, preferably part of a substituent on an alkyl group. Most preferably it is group

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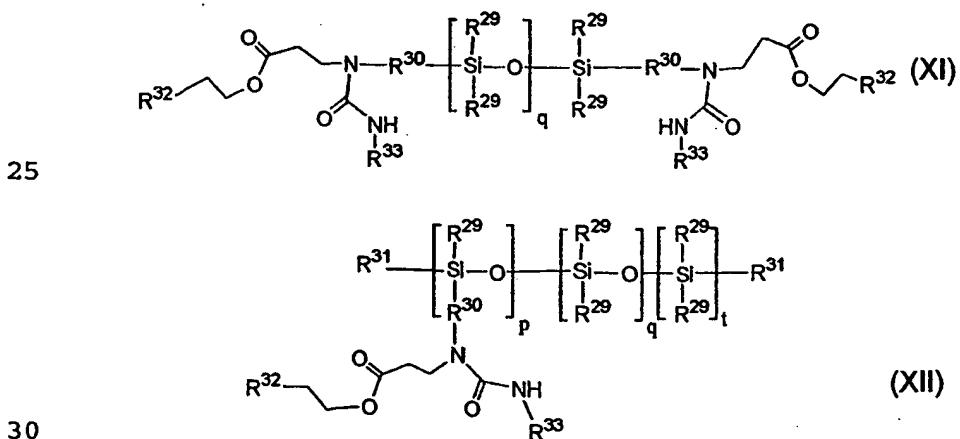
$R^{28}$  which comprises such a polymerisable group. Active hydrogen groups may react with isocyanate groups to form urethane, ureido or thiourea linkages.  $R^{28}$  is preferably alkenylphenyl, allyl, 2-(meth)acryloyloxyethyl, isocyanatoalkyl or isocyanatoalkylaryllalkyl.

5 Preferably  $R^{27}$  is selected among the preferred groups defined above for  $R^4$ .

10 Where a substituent comprises a polymeric moiety, this may be the homo- or co-polymerisation product of a compound of the general formula X. Thus a substituent may comprise the product of the polymerisation of an ethylenically unsaturated compound having the general formula X, or the product of the reaction of a compound of the general formula X having at

15 least two isocyanate substituents with a coreactive compound having at least two active hydrogen atoms (e.g. a diamine or diol), or alternatively of a compound of the general formula X having at least two active hydrogens with a coreactive di- or higher-isocyanate compound.

In one preferred embodiment which is a macromer of both first and 20 second aspects, an adduct has the formula (XI) or (XII);



wherein

each group R<sup>29</sup> and each group R<sup>31</sup> is independently selected from the group consisting of hydrogen, C<sub>1-6</sub> alkyl, C<sub>6-18</sub> aryl, C<sub>6-18</sub> aralkyl, C<sub>6-18</sub> alkaryl, and C<sub>2-6</sub> alkenyl, preferably C<sub>1-6</sub> alkyl, most preferably methyl or ethyl;

5 the or each R<sup>30</sup> is independently selected from the group consisting of C<sub>1-6</sub> alkanediyl, C<sub>2-6</sub> alkendiyl and C<sub>2-6</sub> alkynediyl, preferably C<sub>1-6</sub> alkanediyl; the or each R<sup>32</sup> is selected from the group consisting of hydroxyl, hydroxyalkoxy, hydroxy(oligoalkoxy) and a zwitterionic group Z;

the or each R<sup>33</sup> is individually selected from the group consisting  
10 linear and branched alkyl, aryl, alkenyl, and alkynyl groups, cycloalkyl, cycloalkenyl, cycloalkynyl, aralkyl, alkaryl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl, acyloxyalkyl (including alkenoyloxyalkyl), acylaminoalkyl, acylaminocycloalkyl, acylaminoaryl, N,N-diacyl-iminoalkyl groups, any of the above groups not  
15 comprising an ethylenically unsubstituted group being substituted with an isocyanate group;

p is an integer of 1 to 50;

q is an integer of 1 to 500;

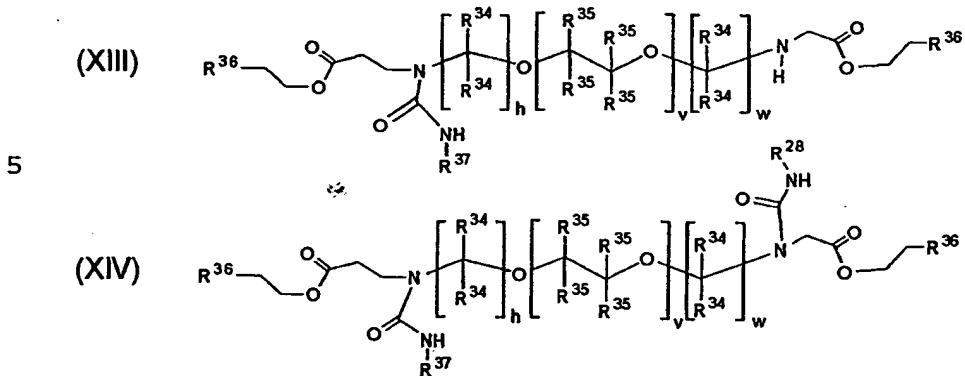
r is an integer of 1 to 50; and

20 t is 0 or 1.

In the formula (XI) and (XII) the order of the siloxyl groups is not intended to represent the specific order within the organosiloxane backbone and in fact these groups can be randomly or specifically ordered within the backbone.

25 Most preferably all of R<sup>29</sup> and any groups R<sup>31</sup> are methyl and R<sup>30</sup> is selected from ethanediyl, propanediyl and butanediyl.

In a further preferred embodiment, compound X has the formula (XIII) or (XIV)



wherein

each group R<sup>34</sup> and R<sup>35</sup> is independently selected from the group consisting of hydrogen, C<sub>1-4</sub> alkyl, C<sub>6-18</sub> aryl, C<sub>6-18</sub> aralkyl, C<sub>6-18</sub> alkaryl; and

15 R<sup>36</sup> is selected from the group consisting of hydroxy, hydrogen, C<sub>2-6</sub> alkenoyloxy, organosilane and organosiloxane groups;

u is an integer of 1-10,

v is an integer of 1-500,

w is an integer of 1-10; and

20 R<sup>28</sup> is an optionally substituted alkyl, alkenyl, alkynyl, aryl, cycloalkyl, cycloalkenyl or cycloalkynyl group

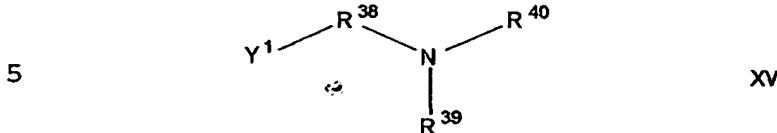
Preferably each R<sup>34</sup> and R<sup>35</sup> is selected from propyl, ethyl, methyl and hydrogen and are preferably all the same, more preferably hydrogen. One of the groups R<sup>35</sup> may be methyl.

25 Preferably any substituent in R<sup>28</sup> is selected from hydroxyl, alkoxy, acyl, acyloxy, acylamino, isocyanate amine, zwitterions, aryl, alkenylaryl and alkenyloxy groups and may comprise polymeric moieties. More preferably R<sup>28</sup> includes a substituent which includes an ethylenically unsaturated group, for instance an alkenoyloxy substituent on an alkyl or on an aryl- or alkyl- aminocarbonyloxy, or aryl- or alkyl- aminocarbonylamino group.

30 Alternatively R<sup>28</sup> includes an isocyanate substituent, preferably in an alkyl, alkaryl, aralkyl or aryl group.

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According to a third aspect of the invention there is provided a hydrophilised organo siloxane prepolymer of the general formula XV



in which Y<sup>1</sup> is an organosiloxane group of the general formula VII defined above;

10 R<sup>38</sup> is a valence bond, or where the divalent group R<sup>14</sup> or R<sup>15</sup> in group VII which is joined to R<sup>38</sup> is a valence bond, is a divalent group selected from straight and branched C<sub>1-12</sub> alkanediyl, C<sub>6-18</sub> arylene, C<sub>7-18</sub>-alkarylene, C<sub>2-12</sub>-alkenediyl and C<sub>2-12</sub>-alkynediyl;

15 R<sup>39</sup> is an organic group comprising an ethylenically unsaturated moiety; and

R<sup>40</sup> is a hydrophilic organic group.

In this aspect of the invention a hydrophilic group is a group which confers increased hydrophilicity on the compound of the general formula XV than the corresponding compound in which R<sup>40</sup> was replaced by a hydrogen atom. Preferably the hydrophilic linear, branched or cyclic group is an alkyl group having one or more hydroxyl, zwitterionic C<sub>1-2</sub> alkoxy, (oligo)hydroxy C<sub>1-6</sub> alkoxy, hydroxyl C<sub>1-6</sub> alkoxy oligo (C<sub>2-3</sub> alkoxy), or C<sub>21</sub> alkoxy oligo (C<sub>2-3</sub> alkoxy) substituents. R<sup>40</sup> is preferably a group of the formula VIII above, or is an alkyl or alkoxy alkyl group having a zwitterionic substituent of the general formula II, IV, V or VI defined above, most preferably of the general formula III defined above.

30 R<sup>39</sup> is an organic group which comprises an ethylenically unsaturated moiety which confers radical polymerisability on the compound XV. The group may include one or more linking moieties such as urea, urethane, thiourea, amide or ester groups in combination with spacers, such as C<sub>1-12</sub> alkanediyl, C<sub>2-12</sub>-alkenediyl, C<sub>2-12</sub>-alkynediyl, arylene and alkarylene via

which the ethylenically unsaturated moiety is joined to the core nitrogen atom.

In one embodiment R<sup>39</sup> is a group R<sup>41</sup> NHCO- in which R<sup>41</sup> is an alkyl, alkenyl, alkynyl, aryl, aralkyl, alkaryl, cycloalkyl, cycloalkenyl or cycloalkynyl group substituted by a group XVI



in which R<sup>42</sup> is hydrogen, C<sub>1-4</sub> alkyl, or -COOR<sup>44</sup> in which R<sup>44</sup> is hydrogen or C<sub>1-4</sub> alkyl,

R<sup>43</sup> is hydrogen, C<sub>1-4</sub> alkyl, or -COOR<sup>44</sup> in which R<sup>44</sup> is hydrogen or C<sub>1-4</sub> alkyl, provided that R<sup>42</sup> and R<sup>43</sup> are not both -COOR<sup>44</sup>, and L is a divalent linker.

L is preferably joined to the carbon to which R<sup>43</sup> is joined by a divalent moiety selected from methylene, a valence bond, -COO-, -CON(R<sup>45</sup>)-, in which R<sup>45</sup> is hydrogen or C<sub>1-4</sub> alkyl, and arylene, which in turn is preferably joined to an alkanediyl, arylene, alkylaminocarbonylamino or arylaminocarbonylamino group.

In another embodiment of this aspect of the invention R<sup>39</sup> is an alkyl group substituted by a group including the ethylenically unsaturated moiety, usually a group of the formula XVI as defined above. For instance R<sup>39</sup> may be a methyl group with the said substituent or a 2-hydroxyethane-1-yl with a 2-substituent of the general formula XVI above.

According to a further aspect of the invention there is provided a first process, suitable for forming a compound of the general formula I as well as other compounds, in which:

in a first step a primary amine compound R<sup>38</sup> NH<sub>2</sub> in which R<sup>38</sup> is selected from linear and branched alkyl, alkenyl, and alkynyl groups, aryl, alkoxy carbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the

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above groups substituted with a zwitterionic group Z an isocyanate group, a hydroxyl group or a polymerisable ethylenically unsaturated group

is reacted with Michael reagent of the formula  $\text{CH}(\text{R}^{39})=\text{CH}(\text{R}^{40})\text{X}^2\text{R}^{41}$  in which  $\text{R}^{39}$  and  $\text{R}^{40}$  are independently selected from hydrogen and  $\text{C}_{1-12}$

5 alkyl groups,

$\text{X}^2$  is an electron withdrawing group selected from the group consisting of carbonyl and sulphone groups, sulphonium and phosphonium salts; and

$\text{R}^{41}$  is selected from linear and branched alkyl, alkenyl, and alkynyl

10 groups, aryl, alkoxy carbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl,

15 oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the above groups substituted with a zwitterionic group Z an isocyanate group, a hydroxyl group or a polymerisable ethylenically unsaturated group to form a secondary amine intermediate  $\text{R}^{38}$

$\text{NHCH}(\text{R}^{39})\text{CH}(\text{R}^{40})\text{X}^2\text{R}^{41}$ , and

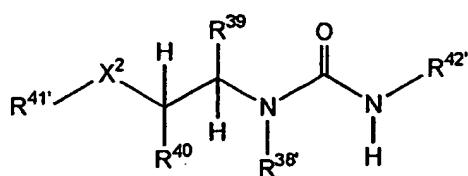
20 in a second step the secondary amine intermediate is reacted with an isocyanate compound  $\text{R}^{42}$  NCO which reacts at the nitrogen atom of the secondary amine group to form a ureido bond, in which  $\text{R}^{42}$  is an alkyl, aryl, alkaryl or aralkyl group optionally substituted by isocyanate or acyloxy groups;

25 in which one of  $\text{R}^{38}$  and  $\text{R}^{41}$  contains an organosiloxane group  $\text{Y}^1$  or an organosilane group  $\text{U}$ ,

one of  $\text{R}^{38}$ ,  $\text{R}^{41}$  and  $\text{R}^{42}$  comprises an ethylenically unsaturated group or is a hydrophilic group.

The product of the two step reaction is believed to have the formula

30 XVII



XVII

35 where  $R^{41'}$  and  $R^{38'}$  are the same as  $R^{41}$  and  $R^{38}$  respectively, or if  $R^{38}$  contains one or more NH substituents or, if  $R^{41}$  contains one or more  $-X^2CH(R^{40})=CH(R^{39})$  substituents, may be the corresponding derivatised groups from the first reaction step, and, if  $R^{42}$  comprises 1 or more isocyanate groups  $R^{42'}$  may be the residue of the oligomerisation of two 40 di- or higher- functional intermediate and isocyanate compounds, otherwise  $R^{42'}$  is the same as  $R^{42}$ .

The definitions of the variable groups in the formula XVII may be such that the compound XVII is a compound of the general formula I as defined above. In some instances one or more of the groups  $R^{38}$ ,  $R^{41'}$  or  $R^{42'}$  may 45 require further derivatisation to form the novel compound of the first aspect. For instance where none of the groups  $R^{38}$ ,  $R^{41'}$  nor  $R^{42'}$  comprises an ethylenically unsaturated group, such a group may be introduced in a further step in which the respective group having an appropriate functional substituent is reacted with a further coreactive ethylenically unsaturated 50 reagent optionally with a linker compound to introduce an ethylenic group. Thus  $R^{38}$ ,  $R^{41'}$  or  $R^{42'}$  may comprise an isocyanate group which may be reacted in a further step with an ethylenically unsaturated compound having an active hydrogen whereby a ureido, urethane or thiourea linkage is formed and the product includes an ethylenically unsaturated group. Other bonds 55 may be generated instead of the urea, this urea or urethane bond, such as amide or ester using conventional reactive compounds.

Similarly where none of  $R^{38}$ ,  $R^{41'}$  nor  $R^{42'}$  is a hydrophilic group, such a group may be introduced in a third step in which the respective group is derivatised with a hydrophilising reactant. Thus an isocyanate group on  $R^{38}$ , 60  $R^{41'}$  or  $R^{42'}$  as the case may be, may be reacted with a hydrophilic compound having an active hydrogen, such as aminofunctional polyethyleneglycol. Again bonds other than urea, urethane or thiourea e.g. amide or ester may be generated instead by use of appropriate reagents.

65 The further reaction to introduce a hydrophilic group, if it involved a di- or higher- functional hydrophilising reagent, and where an organosiloxane group  $Y^1$  which is in  $R^{38}$  or  $R^{41}$  includes one or more amine

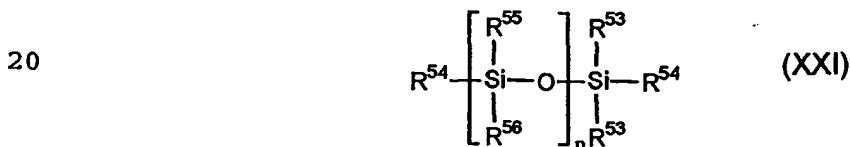
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groups, or one or more substituents  $-X^2CH(R^{40})=CH(R^{39})$ , as the case may be, may be a polymerisation reaction.

Preferably the product of the reaction is not chainlengthened to such an extent that the molecular weight is increased to a level at which it is 5 difficult to solubilise to form a homogeneous solution.

Where the product of the two step reaction is other than a compound within the general formula I it may be a useful intermediate for forming other end products. For instance,  $R^{38}$ ,  $R^{41}$  or  $R^{42}$  may be derivatised to conjugate 10 ligands or surface-binding groups, including hydrophobic, ionic or reactive groups.

A further aspect of the present invention provides a method wherein an organosiloxane bearing at least one primary amine group may be sequentially functionalised, initially by an alkylation step and subsequently by a second step to introduce different functionalities to the molecule. Such 15 functionalities may introduce chemical reactivity, and/or physical properties such as hydrophobicity/hydrophilicity to the molecule. In particular, the invention provides a method in which an amino-functional organosiloxane compound of the formula (XXI)



in which

$R^{53}$ - $R^{56}$  are each selected from  $C_{1-12}$  alkyl,  $C_{2-12}$  alkenyl and  $C_{2-12}$  25 alkynyl,  $C_{6-18}$  aryl,  $C_{7-18}$  aralkyl and  $C_{7-18}$  alkaryl, any of which may be substituted by a primary amine group, and  $n$  is 0-300, provided that at least 1 of the groups  $R^{53}$  to  $R^{56}$  is substituted by a primary amine group,

is reacted in a first reaction with a first reagent to form a secondary 30 amine product (XXV) in which one of the active hydrogens of the said at least one primary amine group is replaced by a group  $R^{57}$  which is joined to the nitrogen atom through a  $>C(R^{58})_2$  link wherein the groups  $R^{58}$  are each hydrogen,  $C_{1-12}$  alkyl or  $C_{1-12}$  alkenyl;

$R^{57}$  is selected from the group consisting of linear and branched alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, aryl, aralkyl, alkaryl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono-, di- and tri- alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl, 5 aminoaryl, alkoxyalkyl, alkenyloxyalkyl, alkynyloxyalkyl, cycloalkoxyalkyl, cycloalkenyloxyalkyl, cycloalkynyloxyalkyl, haloalkoxyalkyl, aralkoxyalkyl, alkoxyaryloxyalkyl, oligoalkoxyalkyl, aminoalkoxyalkyl, mono-, di- and tri-alkylaminoalkoxyalkyl, arylaminoalkoxyalkyl, N-aryl-N-alkylamino-alkoxyalkyl, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, 10 alkylamino, oxacycloalkyl, oxacycloalkenyl, organosilane, organosiloxane, hydroxyalkyl, and hydroxyalkenyl groups and any of the above groups substituted with one or more zwitterionic group  $Z$ ; and

the secondary amine is reacted in a second reaction with at least one second isocyanate reagent whereby the remaining active hydrogen attached 15 to the secondary amine group is replaced by an organic radical joined through a ureido link.

In the definition of  $R^{57}$  any alkyl group or moiety is preferably  $C_{1-18}$  alkyl, any alkenyl group or moiety is preferably  $C_{2-18}$  alkenyl, any alkynyl group or moiety is preferably  $C_{2-12}$  alkynyl, any aryl group or moiety is 20 preferably  $C_{6-24}$  aryl, any alkaryl group or moiety is preferably  $C_{7-24}$  alkaryl and any aralkyl group or moiety is preferably  $C_{7-24}$  aralkyl, any cycloalkyl group or moiety is preferably  $C_{4-24}$  cycloalkyl, any cycloalkenyl group or moiety is preferably  $C_{5-24}$  cycloalkenyl, any cycloalkynyl group or moiety is preferably  $C_{5-24}$  cycloalkynyl.

25 Preferably  $R^{53}$ - $R^{56}$  are each selected from  $C_{1-8}$  alkyl,  $C_{2-8}$  alkenyl and  $C_{2-8}$  alkynyl,  $C_{6-12}$  aryl,  $C_{7-12}$  aralkyl and  $C_{7-12}$  alkaryl, any of which may be optionally substituted by a primary amine group. Of those groups  $R^{53}$ - $R^{56}$ , not substituted by an amine, they are preferably  $C_{1-4}$  alkyl or  $C_{2-4}$  alkenyl, most preferably methyl, ethyl, propyl, and mixtures thereof. Those of  $R^{53}$ - $R^{56}$  30 substituted by an amine are preferably selected from the group consisting of aminomethyl, aminoethyl, aminopropyl, aminobutyl and mixtures thereof.

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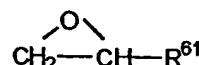
Preferably R<sup>54</sup> comprise the primary amine groups. More preferably R<sup>54</sup> and amino-C<sub>1-6</sub>-alkyl groups, most preferably amino methyl, aminoethyl, aminopropyl, or aminobutyl.

5 In a preferred embodiment the organosiloxane (XXI) has molecular weight in the range of 300-20000 and comprises at least one primary amine group, more preferably 1-20 primary amine groups, more preferably 2-10 primary amine groups, most preferably 2 primary amine groups.

10 In one preferred embodiment, the first reagent is a compound R<sup>60</sup>-X where X is a halogen atom and R<sup>60</sup> = R<sup>57</sup>C(R<sup>58</sup>)<sub>2</sub> and is an optionally substituted C<sub>1-18</sub> alkyl, C<sub>2-18</sub> alkenyl or C<sub>6-24</sub> aryl group, optional substituents being selected from halogen, C<sub>3-12</sub> alkanoyloxy, C<sub>4-12</sub> alkanoyloxy-C<sub>1-12</sub>-alkyl, C<sub>3-12</sub> alkanoylamino, C<sub>4-12</sub> alkenoyloxy, C<sub>4-12</sub> alkenoylamino, carboxylic acid, C<sub>2-12</sub> alkenyl, methacryloyloxy and acryloyloxy.

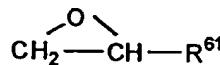
15 Most preferably the first reagent, R<sup>60</sup>-X, is chloromethylstyrene.

15 In another preferred embodiment, the first reagent has the formula



20 where R<sup>61</sup> is selected from the group consisting of hydrogen, C<sub>1-12</sub> alkyl, C<sub>3-12</sub> alkanoyloxy-C<sub>1-12</sub>-alkyl, C<sub>4-12</sub> alkenoyloxy-C<sub>1-12</sub>-alkyl and C<sub>2-12</sub> alkenyl.

Most preferably the first reagent



is glycidoxymethacrylate.

25 The first alkylation step may be performed by any type of alkylation reaction including Michael addition according to the first aspect of the invention.

30 In a preferred embodiment, the second reagent is an isocyanate bearing compound (XXII), whereby the second reaction creates a ureido linkage with the product of (XXI) and the first reagent.

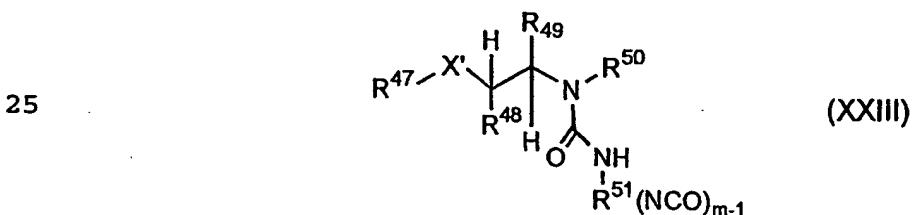
Compound (XIX) may undergo a second reaction with an isocyanate bearing compound (XXII), whereby the second reaction creates a ureido linkage.

Preferably the isocyanate (XXII) has the formula  $R^{51}(NCO)_m$ , where  $R^{51}$  is an m-functional organic radical where m is an integer of 1-10. More preferably m is an integer of 1 or 2.

Preferably  $R^{51}$  is selected from the group consisting of linear and 5 branched alkyl, alkenyl, and alkynyl groups, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, aryl, aralkyl, alkaryl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, acyloxy (including alkenoyloxyalkyl), acyloxyalkyl (including alkenoyloxyalkyl), acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane bonded 10 to the  $(NCO)_m$  through an alkyl group, and organosiloxane groups and any of the above groups substituted with a zwitterionic group Z, or an organosiloxane group.

In the definition of  $R^{51}$ , any alkyl group or moiety is preferably  $C_{1-18}$  alkyl, any alkenyl group or moiety is preferably  $C_{2-18}$  alkenyl, any alkynyl 15 group or moiety is preferably  $C_{2-12}$  alkynyl, any aryl group or moiety is preferably  $C_{6-24}$  aryl, any alkaryl group or moiety is preferably  $C_{7-24}$  alkaryl and any aralkyl group or moiety is preferably  $C_{7-24}$  aralkyl, any cycloalkyl group or moiety is preferably  $C_{4-24}$  cycloalkyl, any cycloalkenyl group or moiety is preferably  $C_{5-24}$  cycloalkenyl, any cycloalkynyl group or moiety is 20 preferably  $C_{5-24}$  cycloalkynyl.

The reaction of (XXII) with compound (XIX) forms a compound having the formula (XXIII)



wherein m=1-10, preferably 1-5 most preferably 2.

In one particularly preferred embodiment,  $R^{51}$  comprises a site of 30 unsaturation, most preferably an isocyanate group capable of crosslinking to another compound of general structure (XIX), another compound, polymer or group, or alternatively a substrate as defined hereinbefore. Said site of unsaturation may alternatively provide a site at which homo or co-

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polymerisation of a compound (XXII) may occur, for example an ethylenically unsaturated group such as (meth)acryloyloxy.

Most preferably the compound (XXII) is an isocyanate or diisocyanate selected from the group consisting of C<sub>2-30</sub> aliphatic, C<sub>6-30</sub> aromatic and C<sub>6-20</sub> alicyclic diisocyanates C<sub>4-30</sub> allyl isocyanates, C<sub>3-30</sub> isocyanatoalkylacrylates, C<sub>5-30</sub> isocyanato alkylmethacrylates, more preferably preferably allyl isocyanate, dimethyl meta-isopropenylbenzylisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, meta-tetramethylxylylene diisocyanate.

10 Where (XXII) is a diisocyanate compound, the reaction with (XIX) may leave the second isocyanate moiety unreacted. This can then be used to crosslink or chain-extend the compound (XIX). Crosslinking may occur with another adduct (XIX) or compound bearing an active >NH or -NH<sub>2</sub> group. Reaction of the second isocyanate may take place with a compound bearing 15 a hydroxy group to form a urethane linkage.

In an alternative reaction to that between (XIX) and (XXII), the compound (XIX) may undergo a second reaction with a compound (XXIV)

R<sup>52</sup>-Q (XXIV)

20 wherein Q is a halogen atom, preferably chlorine or bromine; and R<sup>52</sup> is selected from the group consisting linear and branched alkyl, alkenyl, and alkynyl groups, alkoxy carbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, aryl, aralkyl, alkaryl 25 alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono-, di- and tri-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl, acyloxyalkyl, alkenoyloxy, alkenoyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the above groups 30 substituted with a zwitterionic group Z.

In the definition of R<sup>52</sup>, any alkyl group or moiety is preferably C<sub>1-18</sub> alkyl, any alkenyl group or moiety is preferably C<sub>2-18</sub> alkenyl, any alkynyl group or moiety is preferably C<sub>2-12</sub> alkynyl, any aryl group or moiety is

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preferably C<sub>6-24</sub> aryl, any alkaryl group or moiety is preferably C<sub>7-24</sub> alkaryl and any aralkyl group or moiety is preferably C<sub>7-24</sub> aralkyl, any cycloalkyl group or moiety is preferably C<sub>4-24</sub> cycloalkyl, any cycloalkenyl group or moiety is preferably C<sub>5-24</sub> cycloalkenyl, any cycloalkynyl group or moiety is preferably C<sub>5-24</sub> cycloalkynyl.

Preferably  $R^{52}$  comprises a site of unsaturation, preferably an ethylenically unsaturated group.

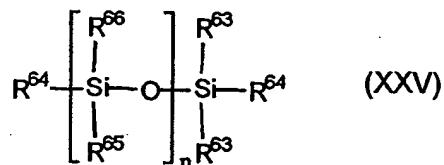
Most preferably  $R^{52}$  is selected from the group consisting of  $C_{1-8}$  alkyl,  $C_{2-10}$  alkenyl, and  $C_{2-10}$  alkynyl groups, particularly styrylmethylene.

10 Most preferably Q is a chlorine atom.

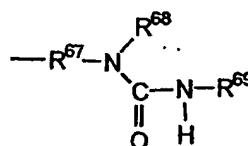
The reaction of (XXIV) with (XIX) generally results in the elimination of HQ, preferably HCl.

In a further aspect of the present invention there is provided an organosiloxane product having formula (XXV)

15



20 in which n is 0-300; and at least one of  $R^{63}$ - $R^{66}$  is a group



25 where  $R^{67}$  is selected from the group consisting of  $C_{1-12}$  alkanediyl,  $C_{1-24}$  alkanediyloxyalkanediyl, (oligoalkanediyloxy)alkanediyl,  $C_{1-24}$  alkanediylcarbonylaminoalkanediyl and  $C_{1-18}$  alkanoyloxyalkanediyl;  $R^{68}$  is a hydrophilic group; and

$R^{69}$  is selected from the same group as  $R^{51}$  as defined above.

Preferably at least 1 of the groups  $R^{64}$  is the group  $R^{67}$ .  
For those groups  $R^{63}$  -  $R^{66}$  which are not  $R^{67}$ , they are selected from  $C_{1-12}$  alkyl,  $C_{1-12}$  alkenyl,  $C_{1-12}$  alkynyl, preferably,  $C_{1-6}$  alkyl, most preferably methyl and are preferably all the same.

27

Any of groups R<sup>63</sup> - R<sup>66</sup> may be substituted with an amine group, preferably a primary or secondary amine group.

Preferably, R<sup>67</sup> is a C<sub>1-4</sub> alkanediyl group, most preferably methanediyl, ethanediyl, propanediyl or butanediyl.

5 R<sup>68</sup> is preferably a hydroxyalkoxyacyl or alkoxyacyl group optionally substituted with a zwitterionic group or a hydroxy group, most preferably R<sup>68</sup> is HOCH<sub>2</sub>CH<sub>2</sub>OC(O)CH<sub>2</sub>CH<sub>2</sub>-.

In a particularly preferred embodiment, R<sup>69</sup> is a group R<sup>70</sup>(NCO)<sub>m</sub> wherein m is 0-10, preferably 1-5 most preferably 1 and R<sup>70</sup> is selected from 10 the group consisting linear and branched alkyl, alkenyl, and alkynyl groups, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, aryl, aralkyl, alkaryl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoarylalkyl, acyloxy (including alkenoyloxyalkyl), acyloxyalkyl (including alkenoyloxyalkyl), acylaminoalkyl, N-diacyl-iminoalkyl 15 groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane bonded to the (NCO)<sub>m</sub> through an alkyl group, and organosiloxane groups and any of the above groups substituted with a zwitterionic group Z.

The overall reaction for the first aspect of the present invention may be carried out in a single or multiple steps, preferably a single or two steps.

20 If Michael addition is to be followed by a functionalisation of the resultant secondary amine a two step reaction may be desirable as this allows work up of a characterisable, pure product after the first step. The reaction, however does not necessarily require an intermediate work-up and a 'one pot' reaction is preferable.

25 The first and third process aspects of the present invention must be carried out in at least two steps, the first being the alkylation reaction and the second being the subsequent functionalisation of the secondary amine product. Again, a 'one pot' reaction is preferable without intermediate work up.

30 The first step (reaction of the α, β-unsaturated group with amine-bearing component or the alkylation of (XXV)) may be performed in a solventless system when one component is able to solubilise the other. Alternatively, an aqueous or organic solvent may be utilised. Preferred

organic solvents include alcohols (including hydroxyalkyl(methyl)acrylate, particularly hydroxyethyl methacrylate), chlorinated hydrocarbons, organosulphoxides, amides and ethers.

Where (I) or (XXV) contains an ester linkage, one prerequisite for the 5 Michael addition step is that the solvent in which the reaction occurs is chosen carefully in order to avoid the possibility of transesterification of the ester linkage in the resulting adduct. Transesterifications are acid or base catalysed reactions and it is likely that the basic structure of the secondary amine in the adduct is sufficient to catalyse the conversion. In particular it is 10 found that the use of methanol as a reaction solvent results in a Michael adduct that has been almost exclusively transesterified, producing the methyl ester of the amine. When isopropylalcohol is used instead of methanol, the transesterification is virtually eliminated with only traces of the transesterified product being detected. Acidity, nucleophilicity and steric 15 hinderance of the alcohol group are all considerations in determining whether the solvent system used will be suitable for the Michael addition.

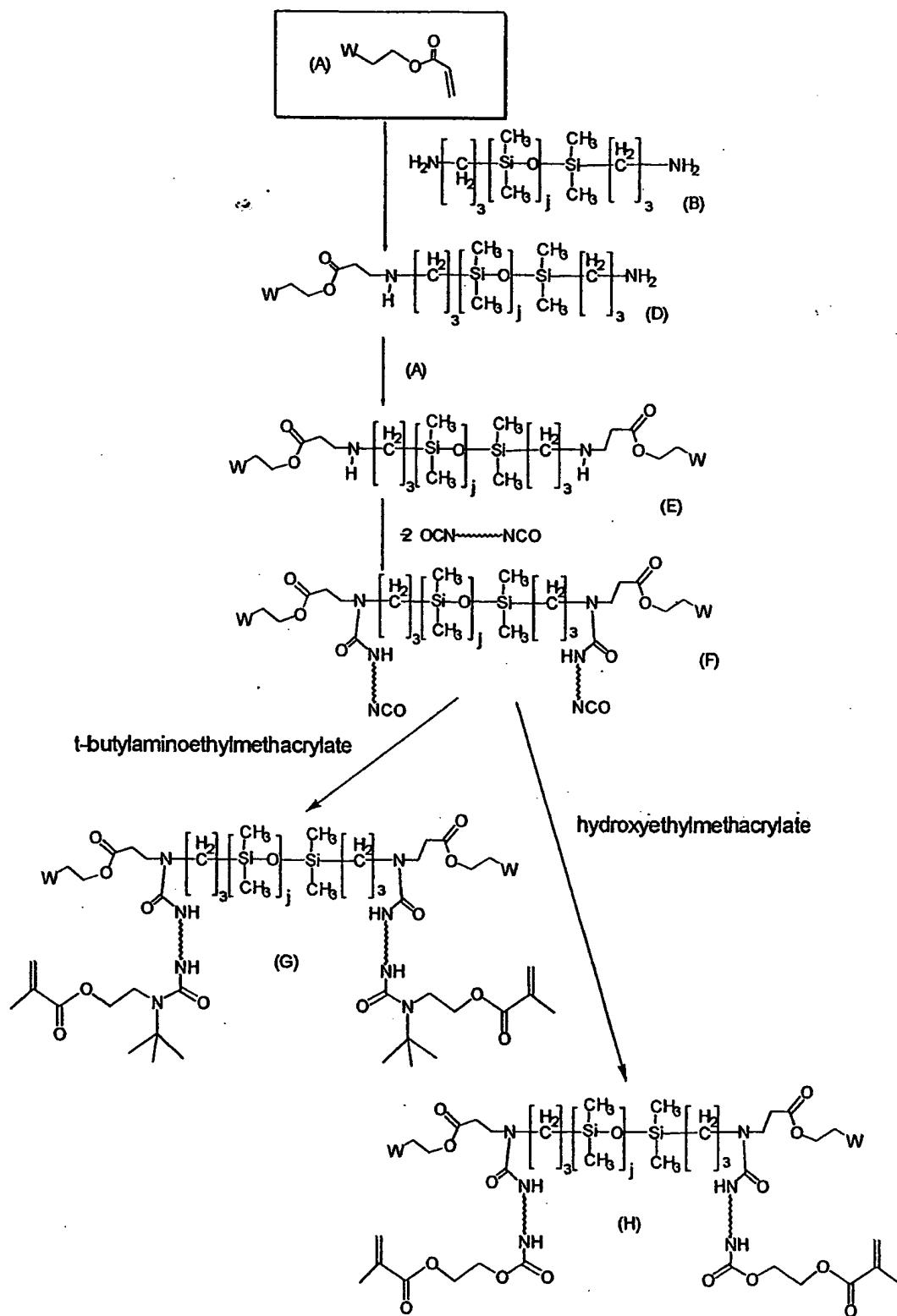
The second step of the reaction (reaction of (XXII) with (XIX) or reaction of (XXII) with (XXV) may be carried out in a solventless system or in aqueous or organic solvents. As the reaction proceeds an organic solvent is 20 usually required. Preferred organic solvents include alcohols, chlorinated hydrocarbons, organosulphoxides, amines and ethers.

Where the second step of the reaction is carried out using a compound (XXIV), the reaction may be carried out in a solventless system or in aqueous or organic solvents. Preferred solvents include amides, for 25 example dimethylacrylamide, and alcohols, for example, isopropylalcohol or hydroxyethyl methacrylate.

A particularly preferred solvent for the first reaction is isopropanol. For the second reaction, the preferred solvents include dimethylsulphoxide, isopropanol, hydroxyethyl methacrylate, tetrahydrofuran, ethanol, or N- 30 methylpyrrolidone.

With regard to the first aspect of the invention, Scheme 1 shows two reaction routes resulting in particularly preferred products.

29



Scheme 1

wherein  $j$  is an integer of 10-400. In scheme 1  $W$  represents a phosphorylcholine group. It could be replaced by another hydrophilic substituent.

In scheme 1, the first two steps may be carried out separately or 5 concurrently depending on the stoichiometry of the reaction. Preferably the production of (E) by the group (A) and (B) occurs in one step. The reaction product may be recovered and the further step of reaction with a reactive group (in the examples shown, a diisocyanate), is carried out.

It should be understood that an organosiloxane, bearing pendant 10 amine groups such as those in compound (XIV) may be used in the above scheme in replacement of compound (B)

For example, if a diisocyanate compound is used to functionalise compound (E) this will produce an isocyanate-functionalised oligomer that could form a block in a segmented polyurethane urea.

15 As shown in the lower part of scheme 1, reaction of a compound of type (F) with a capping compound, for example hydroxyethylmethacrylate or t-butylaminoethylmethacrylate, may be used to produce a methacrylate-terminated oligomer ideal for free-radical polymerisation with other ethylenically unsaturated monomers. This could also be achieved in one 20 step if a Michael adduct of the type (XIX) is reacted with an isocyanate bearing unsaturation in some form. Particularly useful are isocyanates such as dimethylmeta-isopropenylbenzylisocyanate, allylisocyanate or methacryloxyethylisocyanate.

A blend of primary or secondary amine bearing compounds may be 25 added to the  $\alpha, \beta$ -unsaturated group of, for example, compound (A) in order to produce a mixture of macromers. When these are reacted further with an isocyanate bearing unsaturation of some form, for example a pendant isocyanate group, the resultant mixture can be oligomerised or polymerised to produce macromers or polymers comprising a mixture of units having 30 tailored physical properties.

Prior to introduction of a cap, compound (F), for example, could be reacted with a similar or dissimilar group (E), for example. Another amine (either having undergone or not undergone a Michael addition reaction)

31

may be introduced to react with (F) as another way of adding additional entities with desired physical and/or chemical properties into the molecule. The "other amine" is typically any diamine for which the ratio of diisocyanate is adjusted such that some chain extension of compound (F) occurs, prior to 5 capping the molecule. The addition of the "other" amine is prior to cap addition and may be accompanied by further diisocyanate addition to maintain stoichiometry.

As discussed above, the Michael addition reaction may be carried out with either acrylate or methacrylate, although the former is more reactive. 10 This factor may be exploited to generate a methacrylate-functional product by producing a mixed acrylate/methacrylate precursor as in example 13a. Michael addition with an amine-containing group can lead to selective addition to the acrylate functionality. The unreacted methacrylate group can undergo Michael addition with an alternative group, for example an amine 15 containing compound with differing physical properties to the first amine-containing group, or be used as a polymerisable group.

Materials comprising the adducts and products described hereinbefore are of particular utility in medical device manufacture.

The organosiloxane containing adducts of either aspect the present 20 invention, or polymers or copolymers produced by their polymerisation have particular utility in the manufacture of contact and intra ocular lenses. They provide high oxygen permeability and biocompatibility within the ocular environment.

The presence of a zwitterionic component in a polymer provided by 25 polymerisation of an adduct or product of either aspect the present invention improves the biocompatibility of the material compared with non-zwitterionic containing analogues. If, for example, it is desirable to make biodegradable materials, this could be achieved by the incorporation of a suitably labile chain extender, the degradation product being less toxic to the 30 body than a similar compound not bearing a zwitterionic group. Similarly, wear-debris from a non-degradable implant or contact lens of the materials should also be of less risk than a similar material not bearing a zwitterionic group to the body or ocular environment.

The production of a polymer by homo- or co-polymerising an adduct or product of the present invention may be achieved by any known polymerisation method. As described above, an adduct having a site of unsaturation is capable of, for example, free radical polymerisation.

5 The present invention additionally incorporates compositions comprising adduct(s) and/or products of the present invention, and compositions of polymers produced by polymerisation of such an adduct.

It is particularly preferred to copolymerise adducts having ethylenically unsaturated groups with ethylenically unsaturated 10 comonomers. The comonomers preferably include at least one hydrophobic monomer, at least one hydrophilic monomer and at least one cross-linker.

Hydrophilic comonomers are preferably selected from N-vinyl lactams, N,N-dimethyl(meth)acrylamide, (meth)acrylamide, hydroxy-C<sub>1-4</sub>-alkyl(meth)acrylates, vinyl acetate, hydroxy-C<sub>1-4</sub>alkyl(meth)acrylamides and 15 glycerol(meth)acrylate, and mixtures thereof.

Hydrophobic comonomers preferably include at least one organosilyl-group containing monomer, or a fluorinated monomer, or both, and optionally also at least one alkyl or aryl group containing monomer. The organosilyl monomer may be for instance (meth)acrylates of siloxy group substituted 20 alkanols, such as tris(trialkylsiloxy)silylalkyl(meth)acrylates, pentaalkyl- and triaryldialkyl-disiloxanylalkyl(meth)acrylates, alkyldi(trialkylsiloxy)silylalkyl(meth)acrylates, heptaalkyl-cyclotetrasiloxysilylalkyl(meth)acrylates, more preferably tris(trimethylsiloxy)silylpropyl methacrylate. A fluorinated monomer may be 25 selected from vinyl monomers containing at least 3 fluorine atoms, for instance fluoralkyl-(meth)acrylates and -(meth)acrylamides. Specific examples are hexafluoroisopropyl(meth)acrylates and 1,1,2,2-tetrahydroperfluoro-C<sub>4-12</sub>-alkyl-(meth)arylates and -(meth)acrylamides.

Other useful hydrophobic monomers include C<sub>1-24</sub>-alkyl(meth)acrylates, mono- or di-C<sub>3-24</sub>-alkyl(meth)acrylamides, styrene and its derivatives, mono- and di-C<sub>4-24</sub>-alkyl esters of maleic and itaconic acids, C<sub>1-10</sub>-alkyl vinyl ethers, and vinyl esters of C<sub>4-24</sub>-alkanoic acids.

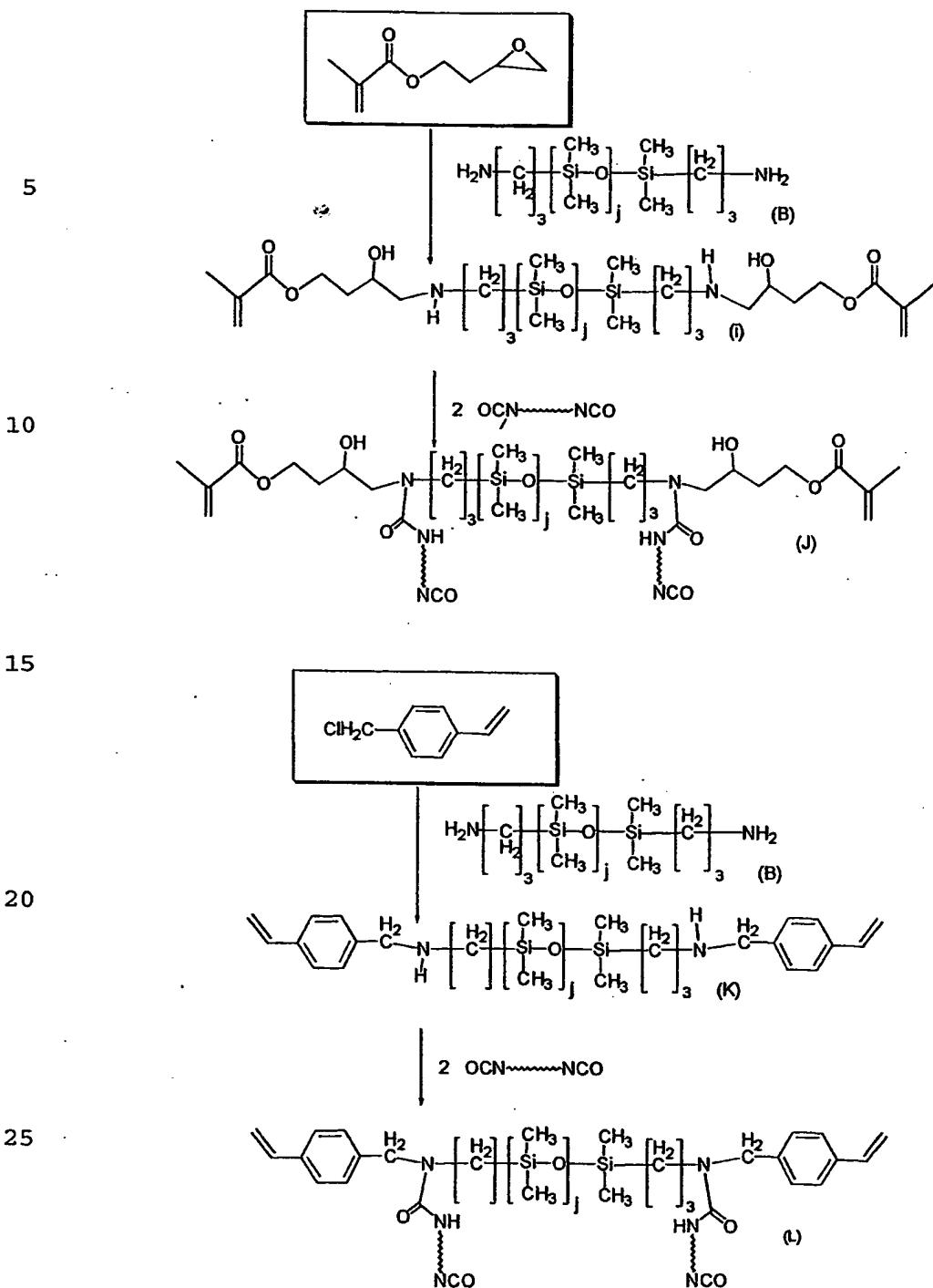
Cross-linking agents have two or more ethylenic groups. They may be water-soluble or water-insoluble. It may be desirable to include one or more water-soluble cross-linking agent, and one or more water-insoluble cross-linking agent. Suitable water-soluble agents are methylene bisacrylamide, ethyleneglycol dimethacrylate and diethylene glycol dimethacrylate. Suitable water-insoluble agents include di(meth)acrylic esters of aromatic diols such as bisphenol A dimethacrylate.

In a copolymerisation, the adduct of the invention is preferably included in the monomer mixture in an weight proportion in the range 10 to 10 95%, preferably 25 to 75%. The hydrophilic monomer is present in an amount in the range 2.5 to 90%, preferably 10 to 25%. The hydrophobic monomer is present in a preferred amount in the range 2.5 to 90%, more preferably 5 to 25%. The cross-linking agent is preferably present in an amount in the range 0.01 to 10%, more preferably 0.1 to 1.0%. Hydrophilic monomer contributes to higher water contents of the final polymer, whilst hydrophobic monomer of the fluorinated or silyl type contributes to increased oxygen permeability which may be of particular where the product is a lens. The level of cross-linking agent affects the water content and physical strength of the polymer. The presence of other hydrophobic monomer 15 contributes also to physical strength.

Scheme 2 shows two particularly preferred embodiments of the second aspect of the invention. The first utilises a glycidoxymethacrylate first reagent with an amino-terminated organosiloxane (B). The oxiran functionality preferentially reacts with the amine groups, leaving the resultant 25 molecule (i) with pendant methacrylate functionalities. Subsequent reaction is shown with an isocyanate group to produce compound (J)

In the second particularly preferred embodiment, the first reagent is chloromethylstyrene. This reacts the terminal amino groups of (B) and eliminates HCl to produce a styryl-functionalised organosiloxane (K). Again, 30 a subsequent reaction with an isocyanate group yields a compound (L).

34



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Scheme 2

The following examples illustrate the working of the present invention.

Starting Materials:

	Material	Code	Supplier
5	Pendant amino-functional PDMS (AEW 1170)	AMS 162	Apollo
	Terminal amino-functional PDMS (AEW 810)	DMS A12	Apollo
	Terminal amino-functional PDMS (AEW 1265)	DMS A15	Apollo
	Terminal amino-functional PEG (AEW 315) (Jeffamine ED 600)	JED 600	Huntsman
10	Ethylene diamine	ED	Aldrich
	Allyl isocyanate	AI	Aldrich
	Dimethyl meta-isopropenyl benzyl isocyanate	TMI	Cytec
	Isophorone diisocyanate	IPDI	Aldrich
15	Hexamethylene diisocyanate	HMDI	Aldrich
	Meta-tetramethylene diisocyanate	TMXDI	Cytec
	Vinylpyrrolidone	VP	Aldrich
	Dimethylacrylamide	DMA	Aldrich
20	t-Butylaminoethyl methacrylate	BAM	Aldrich
	Hydroxyethyl acrylate	HEA	Aldrich
	Ethylhexyl acrylate	EHA	Aldrich
	Butyl acrylate	BA	Aldrich
25	Glycidyl methacrylate	GMA	Aldrich
	Chloromethyl styrene	CMS	Kodak
	Acryloyl phosphorylcholine	APC	Example 2a
	Isopropanol	IPA	Romil
	Acryloxyethyl methacrylate	AEM	Example 12

PEG refers to polyethyleneglycol and AEW refers to amine equivalent weight.

Example 1: Preparation of a Silicone/HEA/TMI Macromer

30 30g of AMS 162 (AEW 1170, Apollo Scientific) was weighed into a 250ml r.b. flask fitted with stirrer, thermometer and nitrogen blanket. 3.0g of HEA was added and a small exotherm (~5°C) was noted. An oil bath was placed around the flask and the temperature raised to 60°C. After 1 h the reaction was cooled to 35°C.

35 <sup>1</sup>H NMR confirmed the loss of the HEA acrylate double bond (5.8(d)/6.1(q)/6.4(d)). Peak assignments (Jeol GSX 400, 399.9MHz, CDCl<sub>3</sub>, ppm): ~0.1 (Si-CH<sub>3</sub>); 0.45 (Si-CH<sub>2</sub>-); 1.50 (Si-CH<sub>2</sub>-CH<sub>2</sub>-); 2.55 (combined multiplet, -CH<sub>2</sub>-NH-CH<sub>2</sub>-); 2.87 (-CH<sub>2</sub>-CO-); 3.71 (-CH<sub>2</sub>-OH); 4.22 (-COO-CH<sub>2</sub>-) 8.0g of DMA (Aldrich) was then added followed by 5.2g of TMI (Cytec Industries Inc.) with a wash of 1.6g of DMA. A 20°C exotherm was noted

and the reaction mixture was then heated to 80°C and held for 1h. The resulting macromer in DMA solvent was cooled and FT-IR spectroscopy used to show the disappearance of the isocyanate component (intense N=C=O stretch at ~2260 cm<sup>-1</sup> absent).

5 Isolation and characterisation of the adduct by <sup>1</sup>H NMR showed additional peaks due to the TMI moiety (Jeol GSX 400, 399.9MHz, CDCl<sub>3</sub>, ppm): 1.59 (s, Ar-C(CH<sub>3</sub>)<sub>2</sub>-); 2.05 (s, a-CH<sub>3</sub>); 4.90/5.29 (-C(CH<sub>3</sub>)=CH<sub>2</sub>); 7.19/7.38 (Ar-H) in addition to some minor peak shifts due to the conversion of the 2° amine to the urea function R<sub>2</sub>N-CO-NH-.

10 Example 2a: Preparation of APC

(2-Acryloyloxyethyl)-2'-(trimethyl-ammoniumethyl) phosphate, inner salt (Acryloyl-phosphorylcholine, APC) was made by a modification of the route described previously by Ishihara *et al.* (*Polym. J.*, 22(3), 355, 1990):

15 All glassware was dried thoroughly before use. 2-Chloro-2-oxo 1,3,2-dioxaphospholane (CCP, Avocado Chemical Co.) (68.3g, 0.48mol, 1.05 equiv.) was weighed into a 250ml self-equilibrating dropping funnel and dissolved in ~50ml of acetonitrile. Hydroxyethyl acrylate (HEA, Aldrich Chemical Co.) (53g, 0.46mole) was measured into a 3-neck 2L r.b. flask, fitted with a thermometer (range -100°C-50°C), the dropping funnel, a N<sub>2</sub> bubbler and a magnetic stirrer. The HEA was dissolved in 700ml acetonitrile and cooled to 0°C using a solvent/CO<sub>2</sub> bath. Whilst stirring, N,N,N',N'-tetramethylene diamine (TMEDA, Aldrich Chemical Co.) (36g, 0.24mol, 1.05equiv.) were added, followed by the dropwise addition of the CCP solution over a 20 minute period. The reaction mixture went cloudy upon 20 addition of the CCP as the TMEDA.2HCl salt formed. The reaction was left to stir for 2 hours.

25

25 The TMEDA.2HCl was filtered off under vacuum and an N<sub>2</sub> atmosphere and washed with acetonitrile (~60ml). The clear pale yellow solution was collected in a 2L Florentine flask. A solvent/CO<sub>2</sub> bath was used 30 to cool the solution to ~0°C before bubbling Trimethylamine (TMA, Aldrich Chemical Co.) (81.53, 1.38mol, 3 equiv.) into the solution, while stirring. The flask was fitted with an air condenser with a balloon attached to the top and stirred at 50°C for 16 hours. Excess TMA was then removed under vacuum

via a solvent/CO<sub>2</sub> cold trap, using a HCl trap, whilst stirring at 40°C. ~300ml of acetonitrile was removed and white solid product of APC was filtered off under vacuum and N<sub>2</sub>.

Weight of product collected = 93.7g @ 73%. <sup>1</sup>H NMR (in D<sub>2</sub>O)

5 confirmed the product had been made (characteristic singlet for -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> @ 3.15-3.22ppm, double bond of the acrylate @ 5.98-6.02ppm (doublet), 6.19-6.26ppm (quartet), 6.44-6.48ppm (doublet)). <sup>31</sup>P NMR (in CDCl<sub>3</sub>) showed a peak @ -0.53ppm as expected.

Example 2b: Preparation of a Silicone/APC/AI Macromer

10 7.4g of APC was weighed into a 250ml r.b. flask fitted with stirrer, thermometer and nitrogen blanket. 18.0g of iPA solvent was added and the mixture was heated to 60°C. The APC completely dissolved at about 50°C. 30g of AMS 162 was added with a wash of a further 7.0g of iPA. The temperature was held at 60°C for 15 min and then raised to reflux (ca. 80°C).

15 After 1h the reaction was cooled to 40°C and 2.1g of allyl isocyanate (Aldrich) added with a wash of 1.4g of iPA. An exotherm was noted and the mixture was heated to reflux for 1h. After cooling, FT-IR spectroscopy confirmed the reaction of all isocyanate by loss of the N=C=O stretch.

20 Removal of the solvent under vacuum to yield a thick gum and subsequent <sup>1</sup>H NMR analysis of this product confirmed the expected structure for the adduct (Jeol GSX 400, 399.9MHz, CDCl<sub>3</sub>, ppm): ~0.1 (Si-CH<sub>3</sub>); 0.46 (Si-CH<sub>2</sub>-); 1.57 (Si-CH<sub>2</sub>-CH<sub>2</sub>-); 2.59 (-CH<sub>2</sub>-COO-); 3.08 (b, CH<sub>2</sub>-N-CH<sub>2</sub> & CONH-CH<sub>2</sub>-); 3.30 (N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>); 3.49/3.8/4.1/4.25 (-COOCH<sub>2</sub>CH<sub>2</sub>OP(OO-)OCH<sub>2</sub>CH<sub>2</sub>-N-); 4.22 (-COO-CH<sub>2</sub>-); 5.05/5.15/ 5.87 (allyl-CH=CH<sub>2</sub>)

Examples 3-10: Preparation of Macromers Based on AMS 162

Following the procedures outlined in examples 1 and 2, the macromers shown in Table 1 were similarly prepared using AMS 162 as the amino-silicone:

Example #	di-B-Unsat. Compound	Isocyanate	Solvent
3	HEA	TMI	iPA
4	HEA	AI	DMA
5	APC	TMI	IPA
6	EHA	TMI	IPA
7	HEA, APC	TMI	DMA
8	APC	TMI	HEMA
9	HEA	TMI	HEMA
10	HEA	TMI	VP

10 Table 1: Silicone Macromers based on AMS 162

Example 11: Preparation of a Silicone/HEA-IPDI-BAM Macromer

15 60.0g of DMS A12 (AEW 810, Apollo Scientific) was weighed into a 250ml r.b. flask fitted with stirrer, thermometer and nitrogen blanket. 8.6g of HEA was added at 17°C and an exotherm to 35°C was observed. The temperature was raised to 60°C and held for 1h after which time  $^1\text{H}$  NMR showed complete loss of the acrylate double bond and peak assignments for the product were much the same as described for the pendant amino-PDMS in example 1, demonstrating Michael-type addition of the acrylate to amine.

20 The reaction mixture was cooled and 13.8g of t-butylaminoethyl methacrylate (BAM) was added followed by 20.0g of N,N dimethylacrylamide (DMA) wash and diluent. 15.7g of isophorone diisocyanate was added at 30°C followed by 4.5g of DMA wash. The reaction was held at 60°C for a further 1h and FT-IR spectroscopy used to show complete reaction of the 25 isocyanate groups (disappearance of the N=C=O stretch at 2258cm $^{-1}$ ).

Example 12: Preparation of a Silicone/APC-JED600/APC-TMXDI-BAM Macromer

30 5.62g of APC was weighed into a 250ml r.b. flask fitted with stirrer, thermometer and nitrogen blanket. 12.0g of iPA was added and the mixture heated to 60°C to dissolve the APC. When a clear solution was obtained a blend of 3.15g of Jeffamine ED600 and 12.65g of DMS A15 in 6.0g of iPA was added. The mixture was heated at reflux for 90 min after which it was cooled and 1.85g of BAM added at 40°C. 3.65g of TMXDI was then added. The mixture exothermed and was held at reflux for 1h. IR spectroscopy 35 showed no isocyanate to be present.

Example 13a: Synthesis of Acryloyloxyethyl Methacrylate (AEM)

5.0g of hydroxyethyl methacrylate was weighed into a 250ml r.b. flask fitted with stirrer, thermometer and nitrogen blanket. 3.88g of triethylamine was then added followed by 80ml of dichloromethane. The mixture was  
5 cooled and 4.15g of acryloylchloride was added dropwise. The reaction mixture turned yellow and after 10 min a precipitate formed. Stirring was continued for 90 minutes. The precipitated material (TMEDA.HCl) was then filtered off and the organic solution extracted with sodium bicarbonate solution. The solution was then dried over anhydrous magnesium sulphate  
10 and after filtration the solvent evaporated to give a pale yellow oil (yield~90%).

<sup>1</sup>H NMR confirms the structure expected for AEM (Jeol GSX 400, 399.9MHz, CDCl<sub>3</sub>, ppm): 1.95 (3H, s, CH<sub>3</sub>-); 4.40 (4H, m, -COO-CH<sub>2</sub>CH<sub>2</sub>-OOC-); 5.31/5.70 (1H each, s, (CH<sub>3</sub>)C=CH<sub>2</sub>); 5.87(d)/6.13(q)/6.45(d)  
15 (CH<sub>2</sub>=CH-)

Example 13b: Preparation of a Silicone/AEM-JED600-IPDI-BAM Macromer

16.4 g of DMS A12 was weighed into a 100ml r.b. flask fitted with stirrer, thermometer and nitrogen blanket. 3.6g of AEM were added with  
20 stirring and the reaction mixture heated to 80°C for 1 h. After this time <sup>1</sup>H NMR showed the complete reaction of the acrylate functionality (multiplets from 5.87-6.45 disappear), whilst the methacrylate groups were intact (two singlets at 5.30 & 5.71 ppm).

6.3g of Jeffamine ED600 and 3.7g of BAM in 10.0g of iPA were then  
25 added with 5.0g of iPA rinse. After stirring for a few minutes 6.6g of isophorone diisocyanate was added with 3.0g of iPA rinse. After the exotherm the reaction mix was heated to 80°C for 1h . IR spectroscopy showed no isocyanate present (no N=C=O stretch at 2258cm<sup>-1</sup>).

Example 14: Preparation of a Silicone/GMA-IPDI-BAM Macromer

30 16.4 g of DMS A12 was weighed into a 100ml r.b. flask fitted with stirrer, thermometer and nitrogen blanket. 2.8g of glycidyl methacrylate was added and the mixture heated for a minimum of 2 h.

7.0g of iPA was then added and the mixture cooled to 40°C. 3.7g of BAM were added, followed by 4.4g of isophorone diisocyanate and a wash of 6.4g iPA. The mixture was heated at reflux for 1h after which time IR spectroscopy showed no isocyanate to be present.

5 Example 15: Preparation of a Silicone/HEA/CMS Macromer

11.7g of AMS 162 was weighed into a 100ml r.b. flask fitted with stirrer, thermometer and nitrogen blanket. 1.16g of HEA was added to this and the mixture heated for 1h at 60°C. <sup>1</sup>H NMR confirmed the Michael-type addition of the acrylate to the amine as described for example 1.

10 After this time, 1.56g of chloromethylstyrene (CMS, Kodak Chemicals) was added and the mixture heated for several hours with nitrogen bubbling through the mixture to ensure degassing of any HCl formed upon reaction. After this time a thick gum was isolated and was shown by <sup>1</sup>H NMR to have CMS extensively reacted at the 2° amine positions of the adduct:

(Jeol GSX 400, 399.9MHz, CDCl<sub>3</sub>, ppm): ~0.1 (Si-CH<sub>3</sub>); 0.45 (Si-CH<sub>2</sub>-); 1.50 (Si-CH<sub>2</sub>-CH<sub>2</sub>-); 2.55 (combined multiplet, -CH<sub>2</sub>-NR-CH<sub>2</sub>-); 2.80 (-CH<sub>2</sub>-CO-); 3.61 (Ar-CH<sub>2</sub>-N-); 3.71 (-CH<sub>2</sub>-OH); 4.22 (-COO-CH<sub>2</sub>); 5.2(d)/5.75(d) (ArCH=CH<sub>2</sub>); 6.7(m)/7.35(m) (Ar-H)

15 Examples 16-28: Silicone Macromers Based on DMS A12

20 Following the procedures outlined in examples 11-13, the macromers in Table 2 were similarly prepared:

Example #	Other Diamine	a,b-Unsat. Compound	Isocyanate	Capping Group	Solvent	
					Group	Hexanol
5	16	-	HEA	TMXDI	BAM	iPA
	17	-	APC	TMXDI	BAM	iPA
	18	-	HEA	TMXDI	BAM	iPA
	19	-	EHA	TMXDI	BAM	iPA
	20	-	APC	HMDI	HEMA	
	21	JED 600	HEA	TMXDI	BAM	iPA
10	22	JED 600	HEA	IPDI	BAM	iPA
	23	JED 600	HEA	HMDI	BAM	iPA
	24	JED 600	BA	TMXDI	BAM	iPA
	25	JED 600	BZA	TMXDI	BAM	iPA
	26	JED 600	APC	TMXDI	BAM	iPA
	27	ED	APC	TMXDI	BAM	IPA/Hexanol
15	28	JED 600	GMA	IPDA	BAM	iPA

Table 2: Silicone Macromers Based on DMS A12

Example 29: Generic Method for Contact Lens Preparation and Evaluation

20 The contact lens formulation (macromer/comonomers/initiator/crosslinker) was placed into a glass vial and the mixture degassed for 10 mins with N<sub>2</sub> before dispensing known amounts into polypropylene contact lens moulds (to give -3.0 D power lenses). The moulds were then sealed and UV cured for 1 hour using a Blak-Ray longwave UV lamp model B100AP.

25 The lenses were removed from the mould by soaking in high purity water for 1 hour. They were then soaked in a 70:30 water IPA solution for 2 hours and in borate buffered saline for a further hour. The lenses were then bottled in buffer. A visual assessment of the lenses was made and this was recorded.

30 Lenses were placed in vials that were filled with buffer solution. They were then sterilised by autoclaving at 120°C for 30 mins. A visual assessment of the lenses was made and this was recorded.

35 The equilibrium water content (EWC) of the lens was determined by firstly removing excess (free) water from the lens surface by use of filter paper. The lenses were then placed on a pyrex dish containing drierite and microwaved for 5 minutes on full power (800 watts) and reweighed. The EWC was then calculated as follows:

$$\text{EWC (\%)} = \frac{\text{hydrated weight of lens} - \text{dry weight of lens} \times 100\%}{\text{hydrated weight of lens}}$$

The oxygen permeability (Dk) of the lenses was determined by use of  
 5 Mocon's OptiPerm™ technology according to their SOP#70-006, designed for  
 measuring the Dk value of hydrophilic contact lens materials (Mocon/Modern  
 Controls Inc., 7500 Boone Avenue North, Minneapolis, Minnesota, 55428 USA).  
Examples 30-35: Contact Lens Formulations Using Invention Macromers.

Contact lens formulations were on the basis of mixing the macromers  
 10 of the described invention with NNDMA for further water content enhancement,  
 TRIS for extra silicone content and increase O<sub>2</sub> permeability, EGDMA cross-  
 linked for mechanical properties and Darocur as the UV initiator (see Table 3  
 for typical formulations).

15

Ex. #	Macromer #	Macromer (g)	NNDMA (g)	TRIS (g)	EGDMA (g)	Darocur (g)
30	3	2.0625	2.0536	1.2559	0.0581	0.0519
31	11	4.0624	0.4235	0.5225	0.0503	0.0529
20	32	11	3.2616	1.0325	0.6629	0.0524
33	11	5.0143	1.0314	1.0123	0.0752	0.0753
34	17	1.8291	0.7503	0.5773	0.0532	0.0311
35	23	5.447	0.7604	0.6109	0.0471	0.0585

Table 3: Typical Contact Lens Formulations Using Macromers of the  
 25 Invention

After polymerisation as described in example 29, lenses with the properties described in Table 4 were obtained (n=5 for data):

Example #	Appearance (post UV cure)	Appearance (post autoclave)	EWC (%)	Dk x 10 <sup>4</sup> (ccO <sub>2</sub> /cm <sup>2</sup> /sec. mmHg)
5	30	Clear, colourless	33	*
	31	Clear, colourless	18	99.0
	32	Clear, colourless	30	92.1
	33	Clear, colourless	25	101.6
	34	Clear, colourless	31	81.9
	35	Clear, slight yellow	54	(awaiting)

(\* = Not tested for Dk)

10 Table 4: Properties of Lenses Made Using Macromers of the Invention

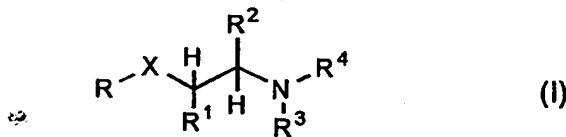
15 Selected silicone lenses were tested for their water permeability and compared to a conventional PHEMA membrane, PHEMA lenses and a commercially available silicone hydrogel lens. The water permeability was determined using a method that employs the use of tritiated water on one side of the lens and its subsequent detection on the other side of the lens allows the relative water permeability to be measured (Fig. 1).

The water permeabilities are seen to be superior to PHEMA hydrogels and indeed better than commercially available silicone hydrogel materials.

Claims

1. A silicon containing adduct having the formula (I)

5



wherein

X is an electron withdrawing group selected from the group consisting of carbonyl and sulphone groups, sulphonium and phosphonium salts;

10 R is selected from the group consisting of linear and branched alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, di-alkylaminoalkyl, N-aryl-N-alkylaminoalkyl, hydroxyalkoxy, alkoxy, alkenyloxy, alkynyoxy, cycloalkoxy, cycloalkenyloxy, cycloalkynyoxy, aralkoxy, alkoxyaryloxy, alkoxyalkoxy, oligoalkoxyalkoxy, di-alkylaminoalkoxy, N-aryl-N-alkylamino-alkoxy, acyloxy, acyloxyalkyl, N-diacyl-iminoalkyl groups, organosilane, organosiloxane, hydroxyaryl, hydroxyalkenyl, hydroxyalkynyl and hydroxy groups and any of the above groups substituted with one or more hydroxyl or zwitterionic group Z, or R-X- is a nitrile group;

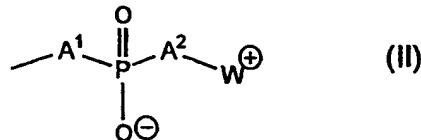
20 R<sup>3</sup> and R<sup>4</sup> are independently selected from the group consisting of hydrogen, linear and branched alkyl, alkenyl, and alkynyl groups, aryl, alkoxycarbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the above groups substituted with a zwitterionic group Z an isocyanate group, a hydroxyl group or a polymerisable ethylenically unsaturated group;

25 R<sup>1</sup> and R<sup>2</sup> are individually selected from hydrogen and C<sub>1</sub>-C<sub>12</sub> alkyl groups; and

30 a first group selected from R, R<sup>3</sup>, and R<sup>4</sup> contains an organosiloxane group Y and/or an organosilane group U,

a second group selected from R, R<sup>3</sup> and R<sup>4</sup> is a hydrophilic group and the third group selected from R, R<sup>3</sup> and R<sup>4</sup> comprises a polymerisable ethylenically unsaturated group or an isocyanate group.

2. An adduct according to claim 1, wherein the said hydrophilic group includes a zwitterionic group Z, which has the general formula (II)



10

in which

the moieties A<sup>1</sup> and A<sup>2</sup>, which are the same or different, are -O-, -S-, -NH- or a valence bond, preferably -O-, and

15 W<sup>+</sup> is a group comprising an ammonium, phosphonium or sulphonium cationic group and a group linking the anionic and cationic moieties which is preferably a C<sub>1-12</sub>-alkanediyl group,

preferably in which W<sup>+</sup> is a group of formula

-W<sup>1</sup>-N<sup>+</sup>R<sup>5</sup><sub>3</sub>, -W<sup>1</sup>-P<sup>+</sup>R<sup>6</sup><sub>3</sub>, -W<sup>1</sup>-S<sup>+</sup>R<sup>6</sup><sub>2</sub> or -W<sup>1</sup>-Het<sup>+</sup> in which:

20 W<sup>1</sup> is alkanediyl of 1 or more, preferably 2-6 carbon atoms optionally containing one or more ethylenically unsaturated double or triple bonds, disubstituted-aryl (arylene), alkylene arylene, arylene alkylene, or alkylene aryl alkylene, cycloalkanediyl, alkylene cycloalkyl, cycloalkyl alkylene or alkylene cycloalkyl alkylene, which group W<sup>1</sup> optionally contains one or more fluorine substituents and/or one or more functional groups; and

25 either the groups R<sup>5</sup> are the same or different and each is hydrogen or alkyl of 1 to 4 carbon atoms, preferably methyl, or aryl, such as phenyl, or two of the groups R<sup>5</sup> together with the nitrogen atom to which they are attached form an aliphatic heterocyclic ring containing from 5 to 7 atoms, or the three groups R<sup>5</sup> together with the nitrogen atom to which they are attached form a 30 fused ring structure containing from 5 to 7 atoms in each ring, and optionally one or more of the groups R<sup>5</sup> is substituted by a hydrophilic functional group, and

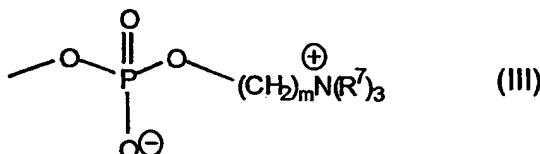
the groups R<sup>6</sup> are the same or different and each is R<sup>5</sup> or a group OR<sup>5</sup>, where R<sup>5</sup> is as defined above; or

Het is an aromatic nitrogen-, phosphorus- or sulphur-, preferably nitrogen-, containing ring, for example pyridine.

3. An adduct according to claim 2 wherein the zwitterionic group of the formula (II), has the general formula (III):

5

10



in which

the groups R<sup>7</sup> are the same or different and each is hydrogen or C<sub>1-4</sub> alkyl, and

m is from 1 to 4,

15 in which preferably the groups R<sup>7</sup> are the same preferably methyl.

4. An adduct according to any preceding claim, wherein X is a carbonyl group.

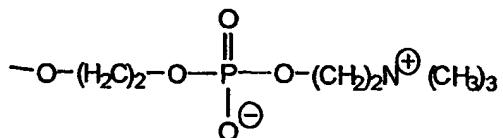
5. An adduct according to claim 4, wherein R is a hydrophilic group, preferably selected from hydroxylalkoxy, hydroxy and poly(oxyalkyl)oxy

20 groups.

6. An adduct according to claim 4, wherein R comprises a zwitterionic group.

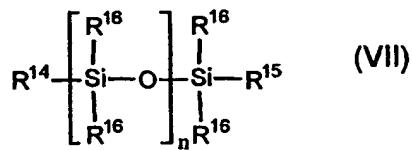
7. An adduct according to any preceding claim, wherein group R has the structure

25



8. An adduct according to any preceding claim, wherein R<sup>1</sup> and R<sup>2</sup> are independently selected from hydrogen and C<sub>1-C4</sub> alkyl, preferably both are hydrogen.

9. An adduct according to any preceding claim, wherein R<sup>4</sup> is an organosiloxane having the formula (VII)



5 in which

$\text{R}^{14}$ ,  $\text{R}^{15}$  and each  $\text{R}^{16}$  are independently selected from monovalent groups selected from hydrogen, branched and straight  $\text{C}_{1-12}$  alkyl,  $\text{C}_{6-18}$  aryl,  $\text{C}_{6-18}$  alkaryl,  $\text{C}_{6-18}$  aralkyl,  $\text{C}_{2-12}$  alkenyl,  $\text{C}_{2-12}$  alkynyl and  $(-\text{OSiR}^{16})_p\text{OSiR}^{16}$ , and divalent groups selected from a valence bond, branched and straight  $\text{C}_{1-12}$ -alkanediyl,  $\text{C}_{6-18}$ -arylene,  $\text{C}_{7-18}$ -alkarylène,  $\text{C}_{12-2}$ -alkenediyl and  $\text{C}_{12-2}$ -alkynediyl, any of which may be substituted by a primary, secondary or tertiary amine group and/or a group  $\text{XCH}(\text{R}^1)\text{CH}(\text{R}^2)\text{NR}^3\text{R}^4$  or a group  $-\text{N}(\text{R}^3)\text{CH}(\text{R}^2)\text{CH}(\text{R}^1)\text{XR}$

$n$  is 0-300 and,

15  $p$  is 0 to 50,

provided that at least one of the groups  $\text{R}^{14}$ ,  $\text{R}^{15}$  and  $\text{R}^{16}$  is a divalent radical which is covalently bonded to the rest of the molecule !

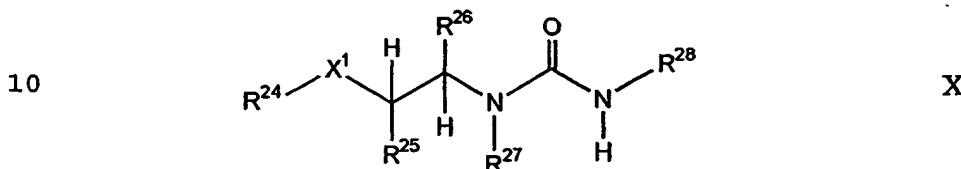
10. An adduct according to claim 9, wherein the groups  $\text{R}^9-\text{R}^{12}$  are individually selected from the group consisting of  $\text{C}_{1-6}$  alkyl groups, preferably  $\text{C}_{1-4}$  alkyl groups, most preferably methyl, and are preferably the same.

11. An adduct according to any of claims 9 or 10, wherein at least one of groups  $\text{R}^{14}-\text{R}^{16}$  comprises a  $-\text{NH}_2$ ,  $-\text{NH}(\text{R}^{17})$ , or  $-\text{N}(\text{R}^{17})_2$  group, wherein  $\text{R}^{17}$  is from linear and branched alkyl, alkenyl, and alkynyl groups, aryl, alkoxy carbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the above groups substituted with a zwitterionic group Z an isocyanate group, a hydroxyl group or a polymerisable ethylenically unsaturated group.

12. An adduct according to claim 9, 10 or 11, wherein R<sup>14</sup> and R<sup>15</sup> are selected from methanediyl, ethanediyl, propanediyl and butanediyl, and are both covalently bound to the nitrogen atom of individual adducts (I).

13. An adduct according to any of claims 1 to 8, wherein R<sup>3</sup> comprises a 5 isocyanate- or (meth)acryloyloxy- substituted alkylaminocarbonyl, cyclolalkylaminocarbonyl or arylaminocarbonyl group.

14. A compound of the general formula



15 in which X<sup>1</sup> is an electron withdrawing group selected from the group consisting of carbonyl and sulphone groups, sulphonium and phosphonium salts;

20 R<sup>24</sup> is selected from the group consisting of hydrogen, linear and branched alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, di- alkylaminoalkyl, N-aryl-N-alkylaminoalkyl, hydroxyalkoxy, alkoxy, alkenyloxy, alkynyoxy, cycloalkoxy, cycloalkenyloxy, cycloalkynyoxy, aralkoxy, alkoxyaryloxy, alkoxyalkoxy, oligoalkoxyalkoxy, di-alkylaminoalkoxy, N-aryl-N-alkylaminoalkoxy, acyloxy, acyloxyalkyl, N-diacyl-iminoalkyl groups, organosilane, organosiloxane, hydroxyaryl, hydroxyalkenyl, hydroxyalkynyl and hydroxy groups and any of the above groups substituted with one or more hydroxyl or 25 zwitterionic groups Z or R<sup>24</sup> X<sup>1</sup>- is a nitrile group;

25 R<sup>25</sup> and R<sup>26</sup> are independently selected from hydrogen and C<sub>1</sub>-C<sub>12</sub> alkyl groups;

30 R<sup>27</sup> is an optionally substituted alkyl, alkenyl, alkynyl, aryl, cycloalkyl, cycloalkenyl or cycloalkynyl group; and

35 R<sup>28</sup> is an optionally substituted alkyl, alkenyl, alkynyl, aryl, cycloalkyl, cycloalkenyl or cycloalkynyl group.

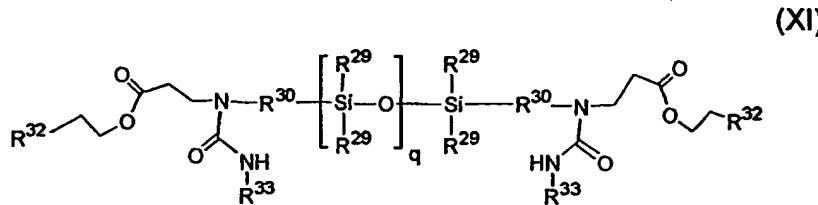
15. A compound according to claim 14 in which R<sup>24</sup> is a hydrophilic group, preferably selected from a zwitterionic or hydroxyl substituted alkoxy, alkoxyalkoxy or oligoalkyoxyalkoxy group.

16. A compound according to claim 14 or 15, in which one of the groups 5 R<sup>24</sup>, R<sup>27</sup> and R<sup>28</sup> comprises a polymerisable group, preferably selected from an ethylenically unsaturated group, an isocyanate or an active hydrogen containing group, preferably part of a substituent on an alkyl group.

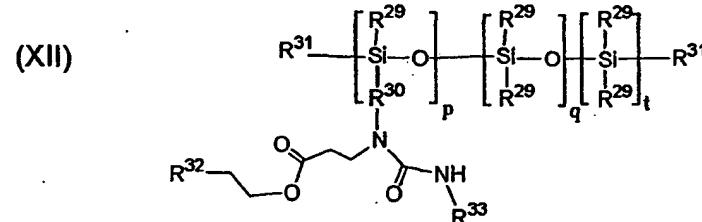
17. An adduct according to any preceding claim which has formula (XI) or (XII);

10

15



20



wherein

each group R<sup>29</sup> and each group R<sup>31</sup> is independently selected from the group consisting of hydrogen, C<sub>1-6</sub> alkyl, C<sub>6-18</sub> aryl, C<sub>6-18</sub> aralkyl, C<sub>6-18</sub> alkaryl, and C<sub>2-6</sub> alkenyl, preferably C<sub>1-6</sub> alkyl, most preferably methyl or ethyl;

the or each R<sup>30</sup> is independently selected from the group consisting of C<sub>1-6</sub> alkanediyl, C<sub>2-6</sub> alkendiyl and C<sub>2-6</sub> alkynediyl, preferably C<sub>1-6</sub> alkanediyl;

the or each R<sup>32</sup> is selected from the group consisting of hydroxyl, hydroxyalkoxy, hydroxy(oligoalkoxy) and a zwitterionic group Z;

the or each R<sup>33</sup> is individually selected from the group consisting linear and branched alkyl, aryl, alkenyl, and alkynyl groups, cycloalkyl, cycloalkenyl, cycloalkynyl, aralkyl, alkaryl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl, acyloxyalkyl (including

alkenoyloxyalkyl), acylaminoalkyl, acylaminocycloalkyl, acylaminoaryl, N,N-diacyl-iminoalkyl groups, any of the above groups not comprising an ethylenically unsubstituted group being substituted with an isocyanate group;

5                   p is an integer of 1 to 50;

q is an integer of 1 to 500;

r is an integer of 1 to 50; and

t is 0 or 1.

19. An adduct according to claim 18, wherein all groups R<sup>29</sup> and any groups R<sup>31</sup> are all methyl and R<sup>30</sup> is selected from ethanediyl, propanediyl and butanediyl.

10                  19. An adduct according to any of claims 1 to 8 wherein R<sup>3</sup> is an organosilane group having the general formula (IX)

15                  
$$\begin{array}{c} (\text{OR}^{16}) \\ | \\ -\text{R}^{15}-\text{Si}-(\text{OR}^{17}) \\ | \\ (\text{OR}^{18}) \end{array} \quad (\text{IX})$$

wherein R<sup>16</sup>, R<sup>17</sup> and R<sup>18</sup> are selected from the group consisting of hydrogen, branched and straight C<sub>1-12</sub> alkyl, C<sub>6-18</sub> aryl, C<sub>6-18</sub> alkaryl, C<sub>6-18</sub> aralkyl, C<sub>2-12</sub> alkenyl and C<sub>2-12</sub> alkynyl;

20                  R<sup>15</sup> is selected from the group consisting of a valence bond, branched and straight chain C<sub>1-12</sub> alkanediyl, straight and branched C<sub>2-12</sub> alkenediyl and straight and branched C<sub>2-12</sub> alkynediyl; and

(IX) is connected to the N atom of (I) through R<sup>15</sup>.

25                  20. process, suitable for forming a compound of the general formula I as well as other compounds, in which:

in a first step a primary amine compound R<sup>38</sup> NH<sub>2</sub> in which R<sup>38</sup> is selected from linear and branched alkyl, alkenyl, and alkynyl groups, aryl, alkoxy carbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-

30                  alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the above groups

substituted with a zwitterionic group Z an isocyanate group, a hydroxyl group or a polymerisable ethylenically unsaturated group

is reacted with Michael reagent of the formula  $\text{CH}(\text{R}^{39})=\text{CH}(\text{R}^{40})\text{X}^2\text{R}^{41}$  in which  $\text{R}^{39}$  and  $\text{R}^{40}$  are independently selected from hydrogen and  $\text{C}_{1-12}$  alkyl groups,

$X^2$  is an electron withdrawing group selected from the group consisting of carbonyl and sulphone groups, sulphonium and phosphonium salts; and

**R<sup>41</sup>** is selected from linear and branched alkyl, alkenyl, and alkynyl groups, aryl, alkoxycarbonyl, alkylaminocarbonyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, alkaryl, aralkyl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono- and di-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl and -aminoaryl, acyloxy, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane and organosiloxane groups and any of the above groups substituted with a zwitterionic group Z an isocyanate group, a hydroxyl group or a polymerisable ethylenically unsaturated group to form a secondary amine intermediate  $R^{38} NHCH(R^{39})CH(R^{40})X^2R^{41}$ , and

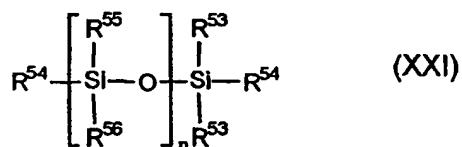
in a second step the secondary amine intermediate is reacted with an isocyanate compound  $R^{42} NCO$  which reacts at the nitrogen atom of the secondary amine group to form a ureido bond, in which  $R^{42}$  is an alkyl, aryl, alkaryl or aralkyl group optionally substituted by isocyanate or acyloxy groups;  
20 in which one of  $R^{38}$  and  $R^{41}$  contains an organosiloxane group  $Y^1$  or an organosilane group  $U$ ,

one of  $R^{38}$ ,  $R^{41}$  and  $R^{42}$  comprises an ethylenically unsaturated group  
25 or is a hydrophilic group.

21. The method according to claim 20, wherein  $R^{39}$  and  $R^{40}$  are selected from hydrogen or  $C_1$ - $C_4$  alkyl groups, most preferably both hydrogen.

22. The method according to claim 20 or 21, in which  $X^2$  is carbonyl.

23. A method in which an amino-functional organosiloxane compound of  
30 the formula (XXI)



in which  $R^{53}$ - $R^{56}$  are each selected from  $C_{1-12}$  alkyl,  $C_{2-12}$  alkenyl and  $C_{2-12}$  alkynyl,  $C_{6-18}$  aryl,  $C_{7-18}$  aralkyl and  $C_{7-18}$  alkaryl, any of which may be substituted by a primary amine group, and  $n$  is 0-300, provided that at least 1 of the groups  $R^{53}$  to  $R^{56}$  is substituted by a primary amine group, is reacted in

5 a first reaction with a first reagent to form a secondary amine product (XXV) in which one of the active hydrogens of the said at least one primary amine group is replaced by a group  $R^{57}$  which is joined to the nitrogen atom through a  $>C(R^{58})_2$  link wherein the groups  $R^{58}$  are each hydrogen,  $C_{1-12}$  alkyl or  $C_{1-12}$  alkenyl;

10  $R^{57}$  is selected from the group consisting of linear and branched alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, aryl, aralkyl, alkaryl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, aminoalkyl, mono-, di- and tri-alkylaminoalkyl, arylaminoalkyl, N-aryl-N-alkylaminoalkyl aminoaryl, alkoxyalkyl, alkenyloxyalkyl, alkynyloxyalkyl, cycloalkoxyalkyl,

15 cycloalkenyloxyalkyl, cycloalkynyloxyalkyl, haloalkoxyalkyl, aralkoxyalkyl, alkoxyaryloxyalkyl, oligoalkoxyalkyl, aminoalkoxyalkyl, mono-, di- and tri-alkylaminoalkoxyalkyl, arylaminoalkoxyalkyl, N-aryl-N-alkylamino-alkoxyalkyl, acyloxyalkyl, acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylamino, oxacycloalkyl, oxacycloalkenyl, organosilane, organosiloxane, hydroxyalkyl,

20 and hydroxyalkenyl groups and any of the above groups substituted with one or more zwitterionic group  $Z$ ; and

the secondary amine is reacted in a second reaction with at least one second reagent which is an isocyanate compound whereby the remaining active hydrogen attached to the secondary amine group is replaced by an organic radical linked through a ureido linkage.

25 24. A method according to claim 23, wherein  $R^{54}$  comprises the primary amine groups, preferably amino- $C_{1-6}$ -alkyl groups, most preferably aminomethyl, aminoethyl, aminopropyl or aminobutyl.

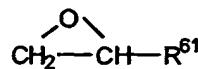
25. A method according to claim 23 or claim 24, wherein the first reagent

30 is a compound  $R^{60}$ -X where X is halogen and  $R^{60} = R^{57}C(R^{58})_2$  and is an optionally substituted  $C_{1-18}$  alkyl,  $C_{2-18}$  alkenyl or  $C_{6-24}$  aryl group, optional substituents being selected from halogen,  $C_{3-12}$  alkanoyloxy,  $C_{4-12}$  alkanoyloxy-

$C_{1-12}$ -alkyl,  $C_{3-12}$  alkanoylamino,  $C_{4-12}$  alkenoyloxy,  $C_{4-12}$  alkenoylamino, carboxylic acid,  $C_{2-12}$  alkenyl, methacryloyloxy and acryloyloxy.

26. A method according to any of claims 23 to 25, wherein the first reagent,  $R^{60}-X$ , is chloromethylstyrene.

5 27. A method according to any of claims 23 or 24, wherein the first reagent has the formula



10 where  $R^{61}$  is selected from the group consisting of hydrogen,  $C_{1-12}$  alkyl,  $C_{3-12}$  alkanoyloxy- $C_{1-12}$ -alkyl,  $C_{4-12}$  alkenoyloxy- $C_{1-12}$ -alkyl and  $C_{2-12}$  alkenyl, most preferably the first reagent is glycidoxymethacrylate.

28. A method according to any of claims 20 to 27, wherein the second isocyanate reagent has the formula  $R^{51} (NCO)_m$ , where  $R^{51}$  is an m-functional organic radical where m is an integer of 1-10.

15 29. A method according to claim 28 in which m is 2.

30. A method according to claim 29, wherein  $R^{51}$  is selected from the group consisting of linear and branched alkyl, alkenyl, and alkynyl groups, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, aryl, aralkyl, alkaryl, 20 alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, acyloxy (including alkenoyloxyalkyl), acyloxyalkyl (including alkenoyloxyalkyl), acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, oxacycloalkyl, oxacycloalkenyl, organosilane bonded to the  $(NCO)_m$  through an alkyl group, and organosiloxane groups and any of the above groups substituted with a zwitterionic group Z, or an 25 organosiloxane group.

31. The method according to any of claims 28 to 30, wherein the isocyanate compound is selected from the group consisting of  $C_{2-30}$  aliphatic,  $C_{6-30}$  aromatic and  $C_{6-20}$  alicyclic isocyanates or diisocyanates  $C_{4-30}$  allyl isocyanates,  $C_{4-30}$  isocyanatoalkylacrylates,  $C_{5-30}$  isocyanato 30 alkylmethacrylates, more preferably allyl isocyanate, dimethyl meta-isopropenylbenzylisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, meta-tetramethylxylylene diisocyanate.

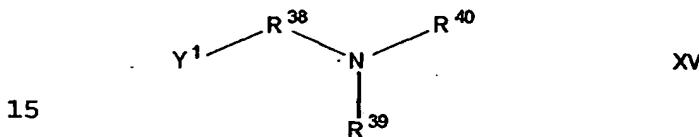
32. The method according to any of claims 20 to 31, wherein the reaction is carried out in a solventless system.

33. The method according to any of claims 20 to 31 wherein the reaction is carried out in the presence of a solvent, preferably an organic solvent

5 selected from C<sub>1-8</sub> alcohols, C<sub>1-8</sub> chlorinated hydrocarbons C<sub>1-8</sub> alkylacrylamides and C<sub>1-8</sub> ethers, preferably secondary C<sub>1-8</sub> or tertiary alcohols.

34. The method according to claim 33, wherein the alcohol is selected from isopropanol, isobutanol, tertbutanol hydroxyalkyl(meth)acrylate, 10 preferably isopropanol.

35. A hydrophilised organo siloxane prepolymer of the general formula XV



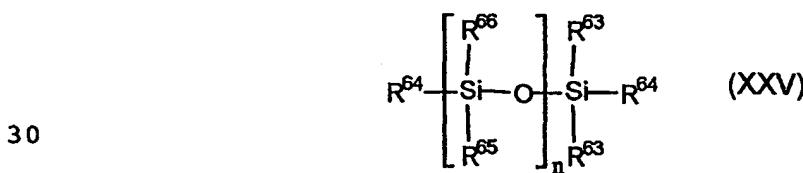
in which Y<sup>1</sup> is an organosiloxane group of the general formula VII defined above;

20 R<sup>38</sup> is a valence bond, or where the divalent group R<sup>14</sup> or R<sup>15</sup> in group VII which is joined to R<sup>38</sup> is a valence bond, is a divalent group selected from straight and branched C<sub>1-12</sub> alkanediyl, C<sub>6-18</sub> arylene, C<sub>7-18</sub>-alkarylene, C<sub>2-12</sub>-alkenediyl and C<sub>2-12</sub>-alkynediyl;

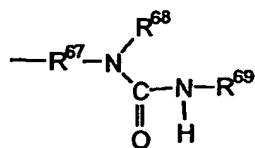
25 R<sup>39</sup> is an organic group comprising an ethylenically unsaturated moiety; and

R<sup>40</sup> is a hydrophilic organic group..

36. An organosiloxane having formula (XXV)



in which n is 0-300; and at least one of R<sup>63</sup>-R<sup>66</sup> is a group



5 where  $\text{R}^{67}$  is selected from the group consisting of  $\text{C}_{1-12}$  alkanediyl,  $\text{C}_{1-24}$  alkanediyoxyalkanediyl, (oligoalkanediyoxy)alkanediyl,  $\text{C}_{1-24}$  alkanediylcarbonylaminoalkanediyl and  $\text{C}_{1-18}$  alkanoyloxyalkanediyl;  $\text{R}^{68}$  is a hydrophilic group; and

10  $\text{R}^{69}$  is a group  $\text{R}^{70}(\text{NCO})_m$  wherein  $m$  is 0-10, preferably 1-5 most preferably 1, and  $\text{R}^{70}$  is selected from the group consisting of linear and branched alkyl, alkenyl, and alkynyl groups, cycloalkyl, cycloalkenyl, cycloalkynyl, haloaryl, haloalkyl, aryl, aralkyl, alkaryl, alkoxyaryl, alkoxyalkyl, oligoalkoxyalkyl, acyloxy (including alkenoyloxyalkyl), acyloxyalkyl (including alkenoyloxyalkyl), acylaminoalkyl, N-diacyl-iminoalkyl groups, alkylaminocarbonyl, 15 oxacycloalkyl, oxacycloalkenyl, organosilane bonded to the  $(\text{NCO})_m$  through an alkyl group, and organosiloxane groups and any of the above groups substituted with a zwitterionic group  $Z$ .

37. An organosiloxane according to claim 36, wherein at least 1 of the groups  $\text{R}^{64}$  is the group  $\text{R}^{67}$  and those groups  $\text{R}^{63}$  -  $\text{R}^{68}$  which are not  $\text{R}^{67}$  are selected from  $\text{C}_{1-12}$  alkyl,  $\text{C}_{1-12}$  alkenyl,  $\text{C}_{1-12}$  alkynyl, preferably,  $\text{C}_{1-6}$  alkyl, most preferably methyl and are preferably all the same.

20 38. An organosiloxane according to claim 36 or 37, wherein  $\text{R}^{67}$  is a  $\text{C}_{1-4}$  alkanediyl group, preferably methanediyl, ethanediyl, propanediyl or butanediyl.

25 39. An organosiloxane according to any of claims 36 to 38, wherein  $\text{R}^{68}$  is a hydroxyalkoxyacyl or alkoxyacyl group optionally substituted with a zwitterionic group or a hydroxy group, most preferably  $\text{R}^{68}$  is  $\text{HOCH}_2\text{CH}_2\text{OC(O)CH}_2\text{CH}_2^-$ .

40. A composition comprising an admixture of an adduct according to any 30 of claim 1 to 19, and/or an admixture of a product according to any of claims 36 to 39, with ethylenically unsaturated comonomers.

41. A composition comprising a polymer produced by polymerisation of an admixture according to claim 40.

42. A composition according to claim 41, wherein the composition is a liquid composition comprising a solvent in which the polymer is dissolved or suspended.
43. An article produced from or coated by an adduct according to any of claims 1 to 19 or 36 to 39 or a polymer as defined in claim 40.
44. An article according to claim 43, wherein the article is a contact lens.
45. A polymer produced by the homo-polymerisation or co-polymerisation of an adduct according to any of claims 1-19, or a product according to any of claims 36 to 38.
- 10 46. A polymer according to claim 45, produced by a polymerisation process selected from free radical, cationic, anionic and metal catalysed polymerisations, preferably free radical polymerisation.
47. A process for coating a surface comprising applying a composition according to claim 42 to the surface of a polymer or metal and substantially removing the solvent.
- 15 48. A polymerisation process comprising the homo-polymerisation or co-polymerisation of an adduct according to any of claims 1 to 19, or a product according to any of claims 36 to 38.

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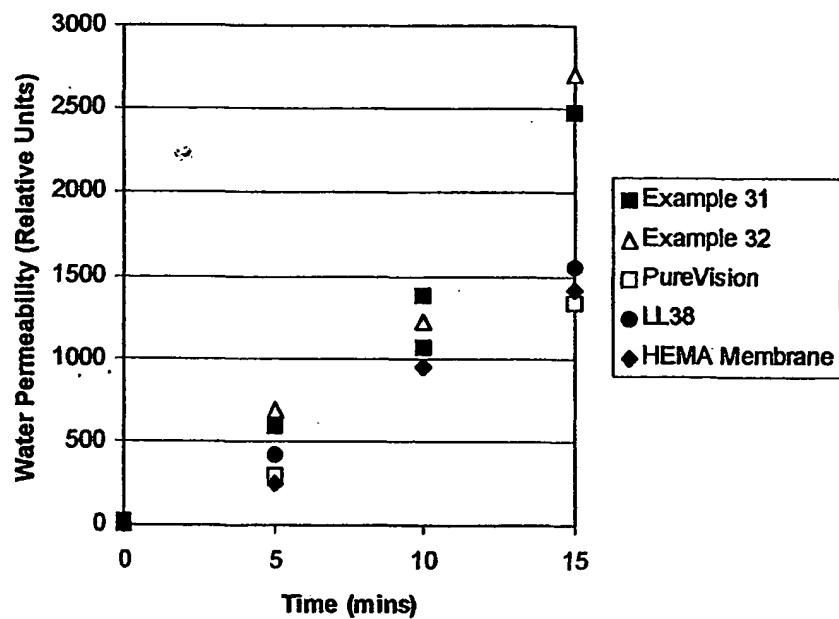


Figure 1

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
EPO, GB 01/00519

A. CLASSIFICATION OF SUBJECT MATTER	
IPC 7	C07F7/08 C08G77/04 C08G77/00 C08G77/26 C08G77/388
	C07F9/09 C07F9/22 C07F7/02 C08L83/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07F C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 933 399 A (WACKER CHEMIE GMBH) 4 August 1999 (1999-08-04) cited in the application page 4, line 38 -page 6, line 32; examples 1,16	1,4-7, 9-13,17, 19,40
X	page 7, line 4 - line 14	41-43, 45-48
Y	the whole document ---	1-13
Y	EP 0 818 479 A (BIOCOMPATIBLES LTD) 14 January 1998 (1998-01-14)  page 1, line 51 -page 2, line 29; claims 3,10,11 page 6, line 10 -page 13, line 53 ---	1-13, 20-22, 36-38, 40-48
		-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

- "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "8" document member of the same patent family

Date of the actual completion of the international search

11 April 2001

Date of mailing of the international search report

9.08.2000

Name and mailing address of the ISA

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Authorized officer

Richter, H

## INTERNATIONAL SEARCH REPORT

Inte  
nal Application No  
PCT/GB 01/00519

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 230 342 A (DOW CORNING) 29 July 1987 (1987-07-29) cited in the application pages 33,34,39: acryl functional siloxanes claims 2-12; examples 1,3 ---	1,20-22, 40,43, 45-48
X	US 4 603 086 A (FUJII HITOSHI ET AL) 29 July 1986 (1986-07-29)  The whole document, in particular column 4, lines 21-28 ---	1,20-22, 40,43, 45-48
Y	EP 0 844 268 A (DOW CORNING) 27 May 1998 (1998-05-27) page 1, line 5 - line 44; claims 1-4; examples 1-9 ---	20-22
Y	EP 0 455 585 A (CIBA GEIGY AG) 6 November 1991 (1991-11-06) cited in the application Makromer A1 page 2; claims 1-3,5-15,26 -----	36-38, 40-48

## INTERNATIONAL SEARCH REPORT

ntional application No.  
PCT/GB 01/00519

### Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: 19 (first occurrence), 35 because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
  
3.  Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  
completely 1-13, 17-22, 23-34, 36-39, partially 40-48

#### Remark on Protest

The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 19 (first occurrence), 35

Dependent claim 19 (1) contains a backreference to a claim 18 which does not exist.

Independent claim 35 refers to a general formula VII. The reference "defined above" is rather vague because the definition of formula VII in claim 9 differs from the definition in the description at page 9, see in particular lines 17-19.

The present statement of claims even in the same group of inventions consists of several attempts to formulate the invention in the form of independent claims in the same category. See for instance independent claims 1 and 35 of the first invention. This makes it difficult, if not impossible, to determine the matter for which protection is sought, and places an undue burden on others seeking to establish the extent of the protection.

From these deficiencies lack of clarity within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of all claims impossible.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: completely 1-13, 17-22, 23-34,  
36-39 partially 40-48

First Invention

claims 1-13, 17-22 concern the silicon containing adduct of formula (I) and preparation thereof.  
Partially, claims 32-34 and 40-48 concern monomer preparation (32-34), a composition containing at least one monomer (40, 42), a composition comprising a polymerised monomer (41), an article prepared from or coated by a monomer (claims 43, 44), homo- or copolymers (45, 46), homo- or copolymerisation (48) and surface coating by use of a composition according to claims 40-42 (claim 51) insofar as the monomer in these claims is the adduct of formula (I).

- 1.1. Claims: completely 23-34,  
36-39; partially claims 40-48

Second Invention

Claims 36-39 and 23-31 relate to the preparation of an organosiloxane of formula (XXI) and its use;  
claims 45, 46: its homo- or copolymers;  
claim 48: its homo- or copolymerisation;  
claims 40-42: composition comprising at least the organosiloxane of formula (XXI);  
claim 41: homo- or copolymers thereof;  
claims 43, 44: an article prepared from or coated by an organosiloxane of formula (XXI);  
claim 47: surface coating by use of a composition according to claim 42

2. Claims: completely 14-16; partially claims 40-48

Third Invention

Compounds of formula X, the presence of Si is not compulsory

claims 45, 46: its homo- or copolymers;  
claim 48: its homo- or copolymerisation;  
claims 43, 45: composition comprising at least the compound of formula (X);  
claim 41: homo- or copolymers thereof;  
claims 43, 44: an article prepared from or coated by a

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

compound of formula (X);  
claim 47: surface coating by use of a composition according  
to claim 42.

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International Application No

PL, GB 01/00519

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
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## INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

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